

ENCYCLOPEDIA OF Glass Science, Technology, History, and Culture

VOLUME 1

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PASCAL RICHET

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VOLUME

1

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**Encyclopedia of Glass Science,
Technology, History, and Culture**

Encyclopedia of Glass Science, Technology, History, and Culture

Volume I

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10.10: Glass, the Wonder Maker of Science; 10.11: A History of
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Preface



When art meets glassmaking: the visit of the Duchess of Berry (1798–1870) in 1824 to the plate-glass factory of the Royal Manufacture of Saint-Gobain as depicted by Édouard Pingret (1788–1869). The stifling heat, the noise of the furnaces, and the danger for the workers of the molten glass poured from the pot and spread with the steel roller on the large table (Chapter 10.9) have all vanished. Only the theatrical aspect of the scene remains, highlighted by the tall curtain, the duchess's light-colored dress echoing the worker's white smocks, and the children watching the show from the balcony. *Source:* Photo courtesy Saint-Gobain Archives.

The *Encyclopedia* has been designed to satisfy the needs and curiosity of a broad audience interested in the nature, properties, fabrication, and history of glass and looking for consistent, comprehensive, and up-to-date information in a single book. More than 100 chapters involving even more glass experts have been written in a perspective that combines the various aspects of this unique material, be they scientific, technological, industrial, historical, or cultural. Whether coming from academia or industry, the authors have in common a long practice of glass. Their goal is to be informative without being pedantic, to be concrete without being boring, and to give a balanced overview of the field – in a word, to allow a large readership to understand both the amazing properties of the vitreous state and its peculiarities compared with those of other states of matter. Excluding the so-called spin glasses and other kinds of disordered physical systems, the *Encyclopedia* restricts itself to what is now termed *structural* glass.

In all chapters, the authors discuss glass from a materials-science standpoint, but their purpose is not to review in any detail the latest advances of interest to specialists only. Rather, in the form of scholarly introductions, it is to present every topic at a uniform level and in a self-consistent manner. In this way, the main points will be grasped and key information of fundamental or practical use will be made available. The neophyte reader will then be able to consult the specialized literature and, in particular, the select bibliography appended to each chapter.

This approach does not imply that only elementary features are presented, but that concepts are appropriately introduced and any technical information clearly explained so as to avoid the common defect underlined in 1911 by the astronomer Percival Lowell (1855–1916) who emphasized in *Mars and its Canals* that “nothing in any branch of science is so little known as its articulation, — how the skeleton of it is put together, and what may be the mode of attachment of its muscles.” Whereas a very few chapters give a flavor of current technicalities involved in glass research, newly investigated topics are also considered with the goal of ensuring that the *Encyclopedia* remains a useful reference over an extended period of time. Although those views that are at this moment very speculative are generally not discussed at length, they may be stated in the final *Perspectives* of the chapters.

Given the diversity of topics treated, the name of *Encyclopedia* (*Kuklos paideia*, cycle of enlightenments, in Greek) is particularly appropriate. The surprising fact is that such a reference work was not existing at all for glass, in general, even though more than hundreds of thousands of encyclopedias have now been devoted to any topic worth of attention, including glass art in particular. The

Encyclopedia consists of 10 sections preceded by a general introduction and concluded by a postface. It begins with glassmaking and continues with structural, physical, and chemical properties. The stage is then set to turn to issues pertaining to light, to the main inorganic glass families, to organically related glasses, to environmental and other industrial issues, and, finally, to the main facets of the rich glass history. Even in more than 100 chapters, it has not been possible to deal with every important topic relevant to glass. A few more chapters would have been welcomed, but their advantages would not have outweighed the inconvenience of a longer publication time, especially for the *Encyclopedia* contributors.

Each section is preceded by a short introduction summarizing in a few sentences the contents of its chapters for helping readers to decide which ones fit their own interest best. Another purpose of these introductions is to show that, from the first to the last, the chapters are telling a consistent story. Although efforts have been made to avoid overlap, some limited duplication was inevitable to make sure that most contributions could be read independently of the others. Of course, boundaries between chapters or sections are not always clear-cut, so that some arbitrariness has been involved in their delineation. And whereas the scientific and technology contents of the chapters will probably speak for themselves, it might be useful to note that historical aspects are dealt with not only in the last section but also elsewhere each time they can help to open deeper perspectives. As for the *Culture* included in the title of the *Encyclopedia*, it is explicitly treated only in the very last chapter but pervades a great many others, for example, in the history section where beautiful pieces of art are in particular reproduced.

At the end of this endeavor, it is now a pleasure to acknowledge (i) the encouragement initially provided by R. Conradt, N.G. Greaves, J. Livage, J. Lucas, B. Mysen, A. Takada, and Y. Yue when the project took shape; (ii) the warm welcome this project received through G. Geiger and A. Lekhwani when submitted to the American Ceramic Society and John Wiley & Sons; (iii) the invaluable help then brought all the way by Reinhard Conradt and Akira Takada through their constant advice, support, friendship, and careful reviewing work; (iv) the great many graphics and pictures neatly prepared by Joël Dyon to highlight the matter presented in numerous chapters; (v) the efforts of 151 authors working in 23 countries who participated in this ambitious endeavor and went responsively throughout an editorial process aimed at ensuring an overall homogeneity of style and content, and incorporated in their texts the relevant historical and cultural aspects evoked by the *Encyclopedia* title; (vi) the thoughtful comments and apt observations provided

by nearly 200 reviewers whose names are included at the beginning of every chapter to recognize publicly their contributions; (vii) the original pictures or help in different matters generously provided by colleagues, friends, and institutions whose names are mentioned at the relevant places; (viii) the Humboldt Stiftung, the Ludwig-Maximilians-Universität, and Donald Dingwell for the fruitful work done in Munich; (ix) the so many things about glass or high-temperature techniques and processes discussed over the years with T. Atake, J.-L. Bernard, Y. Bottinga, R. Conradt, K.-U. Hess, R. Kerner, B. Mysen, G. Ottonello, J.-P. Petitot, J. Roux, A. Sipp, J.F. Stebbins, A. Takada, C. Téqui, and other colleagues too numerous to be mentioned; (x) the Table of ion data compiled by J.F. Stebbins, the help provided at various stages of this study by É. Fareau, B. Gasparyan, K.-U. Hess, A. Hofmeister, K. Meliksetian, B. Mysen, and M. Wolf as well as thoughtful comments by J.M. Parker and R.F. Tournier on the section introductions; (xi) and finally Michael Leventhal who oversaw the project at Wiley, Stefanie Volk for copy editing and Viniprammia Premkumar for smooth and responsive production of the book.

The *Encyclopedia* is dedicated to them and to all people whose efforts throughout the ages made glass the astonishing, ubiquitous material it has become.

Select Additional Reading

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General Introduction

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Figure 1 Obsidian core found in the sixth to fifth millennia BCE Aknashen Neolithic site in Armenia. As indicated by the *flake scars*, large flakes were detached in a single final strike by an experienced stone knapper. Source: Photo P. Richet.

1 A Historical Random Walk

1.1 The Glass Age

“Among the so many, so varied products, which attest to the industrial genius of mankind, there are very few that have uses as numerous as *glass*, whose properties are so wonderful,” pointed out in 1868 Georges Bontemps (1799–1883), a famous nineteenth-century glassmaker [1], who added: “no matter could replace glass in the most important of its uses.” At the same time, the great popularizer Louis Figuier (1818–1894) stated that it would be too long to list “the services that glass provides to science, the arts, industry, domestic needs, to the individual acts of man in society, to the poor and the rich, to the ignorant and to the learned.” Stressing that “household economics, science, civilization, progress and well-being, we owe almost all this to glass,” Figuier concluded that “born with primitive societies, glass will only disappear with civilization” [2].

Certainly, Bontemps and Figuier could not have guessed that organic polymers known as *plastics* would replace mineral glass in some of its traditional uses. Ironically, however, not only has mineral glass found many more, such as light guide in optical fibers (Chapter 6.4) or scaffold for bone regeneration (Chapter 8.4) to name only two of the latest, but most organic polymers are also glasses in the physical sense of the term. Since its very first origins, the vitreous state has thus opened astonishing ways to create original materials, to satisfy the most diverse needs and even to discover the world at large.

Unlike other well-established materials, glass has gone through more developments in the past 50 years than in two millennia from both industrial and technological standpoints. Whether overwhelming in the glazing of skyscrapers or hidden in telecommunication networks, glass has become still more ubiquitous in the modern environment than at Bontemps and Figuier’s time so that claiming that we are now living in the *Glass Age* is not an overstatement [3, 4]. Whereas original glass compositions have, for instance, been designed for innovative lighting, screen, and display applications (Chapters 6.9 and 6.10), even the traditional products used for glazing and containers are now taking advantage of various new functionalities (Chapters 6.7 and 6.8). But what might be the most fascinating modern feature of glass is the way in which the material can be engineered to satisfy the most opposite requirements. Long celebrated for light transmission (Chapter 6.1), glass can be made opaque to a wide range of electromagnetic radiations from infrared to X-ray wavelengths through addition of appropriately absorbing elements (Chapters 3.13 and 6.2). Chemical inertness is

another major traditional asset of glass, which is in contrast purposely avoided in *water glass* (Chapter 7.5) and bioactive glasses (Chapter 8.4) whose usefulness rests on their intrinsically high chemical reactivity. And whereas extremely low impurity levels are required in optical fibers and other optoelectronic devices (Chapters 6.3–6.6), storage of municipal and nuclear waste relies on the capacity of glass matrices to incorporate large amounts of a great many elements (Chapters 9.10 and 9.11).

Additional examples are not needed here to illustrate further the point as they will be found in numbers in the *Encyclopedia*. It is more appropriate to stress that most of these engineering developments have relied on the improved understanding of the glassy state brought by a better knowledge of its physical, chemical, and structural properties. What a long way has therefore been traveled since man made acquaintance with a strange, dark rock differing from all others by its luster and especially, when split into pieces, by its extremely sharp edges that even flint could not match!

1.2 An Economic Forerunner

Obsidian (Figure 1), a natural glass found in volcanic provinces in various parts of the Earth, has been known from time immemorial. From arrowheads (Figure 2) to blades of any kinds and purposes (Figure 3), its unique properties made it so valuable to hunter-gatherers that it was the very first item to be extensively exchanged over long distances [5]. Well before any man-made object was produced, obsidian thus embodied at an early stage of human evolution the economic notion of competitive advantage, which eventually resulted in its real trade (Chapter 10.1). At the heart of a dynamic corridor between Eurasia and Africa, present-day Armenia played a significant role in this history as a material source for a wide area in the Near East, initially through moving communities that were carrying their tools with them [6]. Armenia is also important because of the new light it has recently shed on the far-reaching issue of the expansion of archaic *Homo sapiens* out of Africa.

According to a claim often made, this expansion followed the important technical change from bifacial to Levallois technique of stone knapping (Figure 3, cf. [7] for their differences). At the Nor Geghi-I site, near Yerevan, both types of tools actually coexist within alluvial sediments sandwiched in between lava flows dated to



Figure 2 The delicate stone knapping of an arrowhead made possible by obsidian in Pre-Colombian present-day Arizona. Source: Photo courtesy Alexandra Navrotsky.

441 000 $\pm$ 6 000 and 197 000 $\pm$ 7 000 years [8]. From a fundamental standpoint, the synchronic use of both techniques by a single human group at this site thus indicates instead that, after human dispersion, the transition occurred independently within geographically distinct areas. From a practical standpoint, the change allowed better tools to be obtained so much faster from a large core (Figure 1) and with little waste. One could in fact conclude from the incredibly high abundance of artifacts buried in a Middle-Paleolithic site such as Barozh 12 [9], next to the Arteni Complex Volcano (Eastern Armenia), that the concept of disposable object was born with obsidian in the Paleolithic!

Man-made glass appeared considerably later, only three and a half millennia ago in the Late Bronze Age in a wide area ranging from the Near East to Egypt and Greece (Chapter 10.2). The vividly colored but expensive material newly produced was originally the preserve of elites who had recognized its aesthetic and practical interest. After 15 centuries of technical improvements and decreases of production costs, it became a basic commodity in the Roman Empire as acknowledged by Petronius (first century CE) in the *Satyricon* where one of his characters uttered: “You will forgive me if I say that personally I prefer glass; glass does not smell. If it were not so breakable I should prefer it to gold; as it is, it is so cheap” [10]. This chemical inertness achieved at reduced cost was of course one of the early assets of glass. As we now know, others were resulting from its lack of long-range atomic order, which makes forming in the most diverse shapes and sizes possible, produces optical isotropy, gives much flexibility in terms of raw materials and coloring elements thanks to the almost limitless extent of its solid solutions, and is at the source of mechanical properties in principle limited only by the strength of interatomic bonds thanks to the lack of weak grain boundaries.

How was it figured out that glass could completely lose its vivid colors, which first attracted man’s interest, we do not know. The transparency now so closely associated

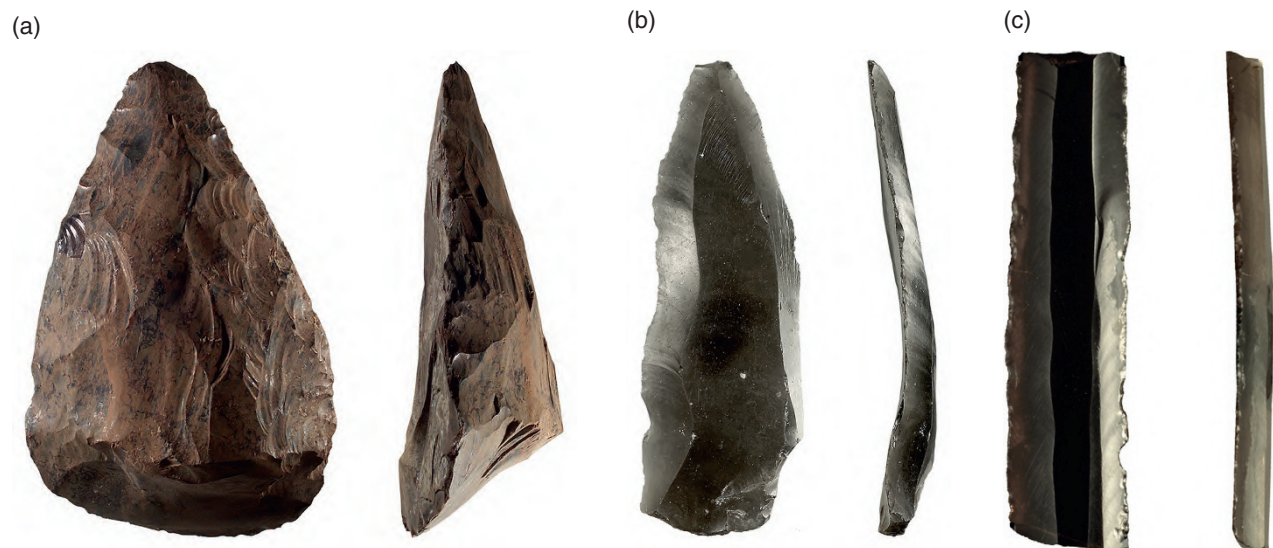


Figure 3 The striking stone-knapping difference between a biface (left) and Levallois point and blade, all made from obsidian (right); length: 20 cm: (a) Acheulean hand axe produced by serial removal of small flakes with a soft hammer (Kuchak-3 open-air site, Aparan Depression, Central Armenia); (b) Levallois Mousterian point, with its plano-convex profile, produced before the reparation of core convexities, and the recurrent method, in which multiple Levallois flakes are detached before reparation (Barozh-12 open-air site, Ararat Depression, Eastern Armenia); (c) Regular flake of the Chalcolithic period produced by pressure flaking from a prismatic core with the aid of a lever (Mastara-1 settlement, Ararat Depression). Source: Photos courtesy Boris Gasparyan.

with glass was first achieved for very special pieces such as cups made in Achaemenid Persia in the fifth century BCE (Chapter 10.0, Figure 1a). But it took several more centuries before transparency became common. The existence of pure, natural carbonates commonly termed natron was the key ingredient to achieve it at a large scale at the beginning of our era [11]. Especially in the Levant, the competitive edge acquired by glassmakers thanks to this substance was such that it led to the establishment of a world market: finished items and glass ingots were traded along well-established commercial routes to be exported as far as East Africa and India [12], the ingots to be shaped locally in small workshops (Chapter 10.3). A first glimpse at globalization?

1.3 A Multifaceted Material

Glass has always aroused much curiosity by its virtue of embodying almost unlimited possibilities for transforming matter. Until the end of the nineteenth century, industrial illustrations of such transformations were the metamorphoses undergone by the large glass pieces that were first blown before being opened and flattened to yield flat panes with the neat fire finish required for transparency (Chapter 10.8). Nowadays, who has never been captivated by the work of a blower, by the action of a delicately controlled fire that gives birth to the most surprising shapes and, in a way, makes the material living for an instant? Even the proverbial brittleness of glass is part of this powerful imaginative world: its fracture indeed seems as unpredictable as it is dramatic, as illustrated by a tempered drinking glass suddenly exploding after several bounces when falling onto the ground.

To this kind of amazement also contributed early the miracles wrought by glass ever since it first restored sight to visually impaired people in the thirteenth century (Chapter 10.10). It is thus no wonder that Leonardo da Vinci (1452–1519) devoted efforts to design a device for machining eyeglasses. Shortly after, the transparent glazing of windows opened houses on the outside world at about the same time as the telescope and the microscope led to the discovery of the universe from the infinitely large to the infinitely small (Chapter 10.10). Grinding of optical lenses was then extensively practiced by Galileo Galilei (1564–1642) himself and considered a trade worth earning a living by the eminent philosopher Baruch Spinoza (1632–1677). That glassmaking had something special is actually indicated by the fact that, in France, it was long the only trade that the nobility could practice as *gentlemen glassmakers* without losing its special status.

To acknowledge all what civilization was owing to this material, the polymath and glassmaker Mikhail Vasilyevich Lomonosov (1711–1765) wrote in Russia a long poem entitled *Letter on the use of Glass*. “A whole year would hardly suffice me to reach the end of worthy praise for Glass” [13], Lomonosov thus claimed when mentioning not only the telescope, the microscope, or the barometer, but also the thrilling electrical researches of his time based on the accumulation of charges on the glass disks of electrostatic machines (Chapter 10.10). Such was the interest raised by the *vitreous* (positive) and *resinous* (negative) electricities “that people of all genders and ranks were then begging for the favor of being subjected to electric shock, to the point that the noble and courageous Professor Georg Matthias Bose (1710–1761) said with philosophical heroism: *I would not regret dying of an electric shock, since the account of my death would provide the subject of an article in the Memoirs of the Royal Academy of Sciences of Paris*” [14]. Could this admirable *philosophical heroism* have been elicited by a material other than glass?

At the same period, glass became the source of another kind of emotions when the famous Benjamin Franklin (1706–1790) was inspired by “the sweet tone that is drawn from a drinking glass, by passing a wet finger around the rim” [15] to design in 1761 the *glass armonica* whereby it was a set of overlapping wet glass cones of different sizes that was rotating to emit a *sweet, ethereal, or pathetic* tone through the friction of fingers. The instrument met with rapid success such that, beginning with Wolfgang Amadeus Mozart (1756–1791) [16], quite a few great composers wrote short pieces for it. The fashion for glass was such that a German living in Paris named Beyer presented in 1785 to the Académie des Sciences his *forte-piano* with glass plates, acted upon by wool-covered hammers, which Franklin christened *glass-cord* [17]. And it was a flute made from lead-crystal glass that the Parisian instrument maker Claude Laurent (d. 1848) patented in 1806 and produced in white, cobalt-blue, and uranium-green hues; in spite of its weight, its musical qualities and reduced temperature-induced pitch changes ensured its popularity for several decades [18].

This select series of anecdotes probably makes it unnecessary to emphasize again the importance of glass in daily and social life stressed above by Bontemps and Figuier. It might in contrast be useful to mention that the antique tradition or ornamental glass was revived at the same period by Georges Frédéric Strass (1701–1773), who became the French King’s jeweler, when he invented *strass*, or *rhinestone*, a high-lead crystal glass bearing various metal oxides that is still made today to imitate precious stones.

1.4 The Silica Paradoxes

1.4.1 Biogenic Silica vs. Flint

Historically, glass owes its importance to silicates. But what substances could have replaced silicate glasses in their diversity of uses on a silicon-free planet? The question would be moot if carbon – the next of kin of silicon in the Periodic Table – and, therefore, life and human beings would have also been lacking. More seriously, however, reflecting on the origin of the silica sources used in glassmaking is not a futile exercise.

It is not widely known that 15 billion tons of *biogenic* silica glass are yearly produced in seawater by diatoms, sponges, and some other living organisms. Such a biological production has major effects on the Earth's global ecosystem and has now become a *biomimetic* source of inspiration for designing wholly new materials (Chapter 8.1). Interestingly, biogenic silica also had noteworthy implications for glassmaking because of its recycling into the opal or microcrystalline quartz of *flint*. Flint, or *chert* as it is called in geology, is commonly found as abundant nodules horizontally embedded in limestone (Figure 4). Its deposition thus requires carbonate

dissolution followed by silica precipitation and, thus, percolating waters undersaturated with respect to calcium carbonates but oversaturated with respect to silica. Without going into the details of the process and of its control by pH and geological context [19, 20], it will suffice here to state that biogenic silica accumulating at the bottom of the sea is the source of the dissolved silica that reprecipitates as flint. And it happens that flint was the raw material used in England from the seventeenth century to remedy the lack of sand pure enough for making optical glass and luxury ware (Chapter 10.10).

In passing, one can also note that silica has been biogenically produced relatively late in evolution compared with calcite and aragonite, the main CaCO_3 polymorphs, but then met with immense success especially with diatoms. A major reason was the advantages of an amorphous compared with a crystalline substance in terms of optical or mechanical properties for the materials protecting the living organisms (Chapter 8.1); amorphous calcium carbonates do exist, but they serve instead as intermediate reaction steps, which are short lived and thus end up crystallizing [21], which is not surprising as molten CaCO_3 is

Figure 4 The abundant beds of black flint present in a 80-m high limestone cliff of the English Channel at the Pointe du Chicard in Yport (Normandy). Same beds of the Upper Cretaceous used in the past for making *flint* glass in England on the other side of the Channel. Height visible on the picture: 10 m. Source: Photo P. Richet.



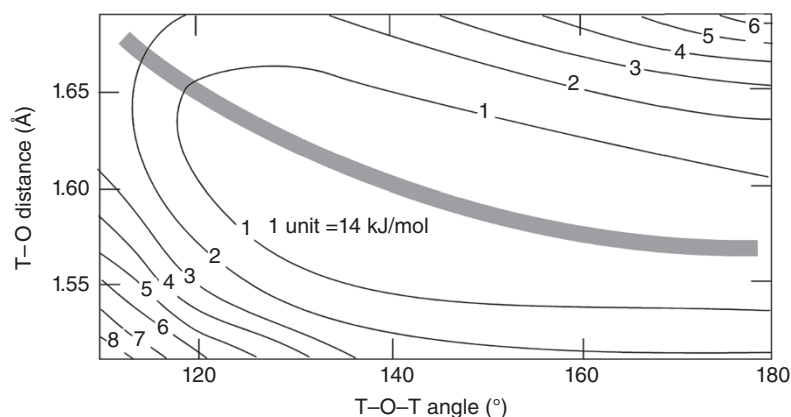


Figure 5 The strong contrast between the potential energy changes induced by variations of Si-O distances and S-O-Si angles indicated by the calculated surfaces of constant energy of $\text{H}_6\text{Si}_2\text{O}_7$ clusters. Source: After [23].

not itself a good glass-forming liquid. Interestingly, formation of biogenic silica would have first been a way to evacuate toxic Si at too high concentrations from cells. By a twist of evolutionary history, it would have become a protecting device so efficient for organisms [22] that it has since then played a major role in the global ecosystem, causing, for instance, the Si concentrations to be so low in seawater.

1.4.2 A Quantum-Chemical Factory: The Production of Silica Sand

Although glassmaking would have been possible without sand, it is unlikely that flint would have led to the invention of glass as it requires thorough grinding to become a reactive raw material. Regardless of grinding costs, it is also doubtful that flint would have been a silica resource widespread and convenient enough for an expanding glass industry. The fundamental importance of silica sand thus remains undisputed. Geologically, sand is produced via the weathering of granite and related SiO_2 -rich igneous rocks. The most abundant rock of the Earth's crust, granite is made up of quartz and alkali $[(\text{Na},\text{K})\text{AlSi}_3\text{O}_8]$ and plagioclase $[(\text{Na}_x\text{Ca}_{1-x})\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8]$ feldspars. Whereas feldspars progressively transform into clay under the action of meteoric waters, quartz resists and accumulates as sand either on the spot or downstream.

The very presence of quartz at the Earth's surface appears to be a clear geochemical anomaly, however, which thus deserves some explanation. With typical 75 wt % SiO_2 , the melts from which granite crystallizes represent the end products of *magma differentiation* (Chapter 7.2). Owing to their very high viscosities, they rarely rise up to the Earth's surface to erupt as obsidian flows but crystallize slowly instead at some depth to yield large-grained rocks. These melts are the last produced after partial crystallization of primary magmas, which form themselves deep in the Earth's mantle by partial melting of SiO_2 -poor, MgO-rich rocks (~45 wt % for both oxides, along with ~7 % FeO, 2 % Al_2O_3 , 1 % CaO, and a few % at most alkali oxides). Because oxygen bonds more

strongly with silicon than with the other elements (Table A.1), one might think that SiO_2 -rich minerals should be the most refractory. As a result, the SiO_2 content of primary magmas should be lower than that of their source rock and decrease further through partial crystallization on their way up to the Earth's surface. Such a trend is opposite to the SiO_2 increase observed. It is in contrast consistent with the fact that cristobalite, the high-temperature polymorph of SiO_2 at room pressure, is less refractory than lime (CaO), periclase (MgO), and even forsterite (Mg_2SiO_4) whose melting temperatures are about 600, 800, and 175° higher than the 2000 K of cristobalite, respectively.

The paradox lies in the fact that bond strengths are usually considered within the framework of ionic forces, which are by definition nondirectional. Now, directionality is an inherent feature of Si-O bonding in view of its markedly covalent character. Because electron delocalization through polymerization and creation of Si-O-Si linkages is not large enough to constrain geometrically the arrangements of the SiO_4 tetrahedra, the same energy variations are, for instance, caused in $\text{H}_6\text{Si}_2\text{O}_7$ clusters by a small 0.02 Å change of the Si-O bond length and by a large 20° modification of the O-Si-O inter-tetrahedral angles (Figure 5). Bending of these linkages is thus so easy that configurational rearrangements take place without involving much energy [24]. The fact is most simply illustrated by the transitions of α -quartz and α -cristobalite to their dynamically disordered β -forms near 573 and 250 °C, respectively. Hence, fusion of these minerals does not require the breaking of bonds involved in ionic crystals. The SiO_2 enrichment and resulting quartz crystallization induced by magma differentiation are thus mainly driven by the sp^3 hybridization of silicon orbitals, which causes largely polymerized crystals to melt at temperatures much lower than would be expected from the Si-O and Al-O bond strengths [24]. In other words, the existence of silica sand originates in a quantum-chemical effect, without which glassmaking would not have existed.

2 Some Basic Concepts of Glass Science

2.1 From Metastability to Relaxation

The silica issue illustrates how answers to apparently simple problems can require in-depth analyses for which theoretical concepts presented in various chapters of the *Encyclopedia* should prove useful. To help readers whose knowledge of the glassy state is minimal, however, the rest of this introduction will be devoted to a brief presentation of some basic concepts pertaining to glass and nonequilibrium systems, which will thus not need to be commented upon in specific chapters.

In preamble, it would be useful to define precisely what a glass is before discussing any of its properties. In accordance with its intrinsically disordered nature, however, glass might be pleasantly defined as a material that is difficult to define in an unambiguous or fully consistent manner. In Chapter 10.11, a glass is nonetheless defined as a macroscopically homogeneous amorphous solid whose properties (physical, chemical, or structural) vary with its preparation conditions. Usual definitions differ depending on whether the emphasis is put on the disordered atomic structure of the material or on the existence of a *glass transition* separating a solid material at lower temperature from a supercooled liquid at higher temperatures. Because glass structures depend on the type of system considered, they are described in widely different ways for oxides, metals, or organic polymers so that they do not lend themselves to a brief, general presentation.

Although a glass transition cannot always be observed, its phenomenology and its implications on glass properties are in contrast common not only to all glass-forming liquids, but also to partially disordered systems such as *plastic crystals*. In view of their dual practical and theoretical importance, the main features of the glass transition will thus be summarized here in a qualitative way. Without making any reference to recent advances in the field, the purpose is simply to describe the phenomenology of vitrification and its effects on physical properties, to introduce some of the groundbreaking concepts that have been proposed to account for them, and to highlight some simplifying features thanks to which intrinsically complex glass problems become more tractable.

A main source of difficulty is that the *time* parameter must be considered because of the kinetic nature of the glass transition. In the backdrop is the way in which the Gibbs free energy of a glass-forming liquid would be minimized under given experimental conditions and, thus, the kinetics at which physical properties *relax* after changes in intensive thermodynamic variables (Chapter 3.7). The largest and most rapid decrease of the Gibbs free energy would of course be ensured by crystallization. To bypass it, it has been known from time immemorial that a melt must be cooled rapidly enough.

Other things being equal, vitrification is favored by large freezing-point depressions near eutectic compositions, which result in increased viscosities and reduced thermodynamic driving forces for crystallization.

With very few exceptions (e.g. [25]), however, supercooled liquids do crystallize more or less rapidly upon prolonged annealing. Perhaps also influenced by the early twentieth-century conception that glasses were supercooled liquids (Chapter 10.11), a commonly held assumption is that any glass would eventually crystallize. This assumption is in fact plainly contradicted by the 4.6-billion year old glasses found in meteorites (Chapter 7.1). What has ensured their long-term preservation has been the extremely dry conditions of extraterrestrial space, which have prevented them from weathering. Since their SiO₂-poor compositions would make them prime candidates for ready devitrification, the almost infinite metastability enjoyed by these glasses is especially significant. The crystallization issue will thus be left aside in the following.

2.2 Relaxation: Phenomenological Aspects

Atomic mobility is the hallmark of the molten state as illustrated by the ready flow of a liquid adjusting to the shape of its container. Contrary to crystals where atomic positions are fixed and strongly constrained by long-range symmetry, liquids are characterized by dynamic disorder, i.e. by unceasing atomic rearrangements. This structural incompatibility between a crystal and a liquid makes any progressive transformation of one phase into the other impossible. In contrast, the vitrification of liquids is clearly a continuous process during which disordered structures become frozen in as revealed by progressively increasing viscosities, which eventually becomes so high that the materials have mechanically become a solid.

At high temperatures, the liquid is in internal thermodynamic equilibrium because its properties are time independent and uniquely determined by two intensive variables, usually taken to be pressure and temperature. At high viscosities, however, this simplicity no longer holds true as seen if one exerts a stress on the liquid at constant temperature or change the temperature at constant stress (Figure 6a). For a window glass [26], a constant, equilibrium shear viscosity is, for example, reached more rapidly in the former case than in the latter but this difference does not need to be commented upon here because pressure and temperature changes are of a different nature. Of greater importance is that Boltzmann superposition principle (Chapter 10.11) applies because, if both perturbations are simultaneously exerted, the response of the system is the sum of the two individual responses (Figure 6a).

In practice, temperature changes matter most. When high viscosities are measured at successively lower temperatures and then at higher temperatures (Figure 6b), two conclusions follow: (i) the time needed to reach the

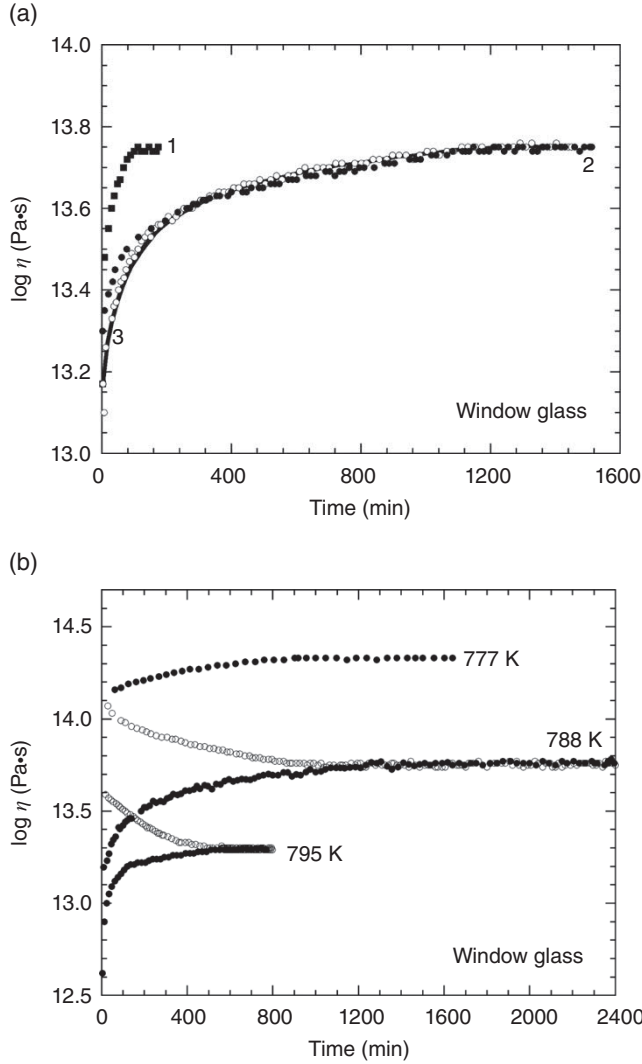


Figure 6 Viscosity relaxation of window glass (Source: Data from [26]). (a) Time dependence of the viscosity at 788 K after: (1) application of a 110 MPa stress; (2) a temperature change from 819 to 788 K with this stress; (3) exerting simultaneously these stress and temperature changes. (b) Attainment of the equilibrium viscosity; sample equilibrated at 795 K, then quickly brought for equilibration at 788 K and at 777 K (open symbols) before following the same procedure for reversing the equilibrium values first measured at 788 and 795 K (open symbols).

constant equilibrium values increases tremendously with decreasing temperatures; (ii) the approach to equilibrium is slower when the sample was previously equilibrated at a lower than at a higher temperature. Hence, the rate at which these changes occur depends not only on temperature but also on the thermal history of the sample, i.e. on the instantaneous structure as well. Because thermodynamic equilibrium is reached when the structure has adjusted to the new intensive parameters, the process is termed *structural relaxation*.

To characterize the rate at which the shear viscosity (η) or any other property Y approaches a new equilibrium value, Y_e , one defines the relaxation time, τ_Y , as

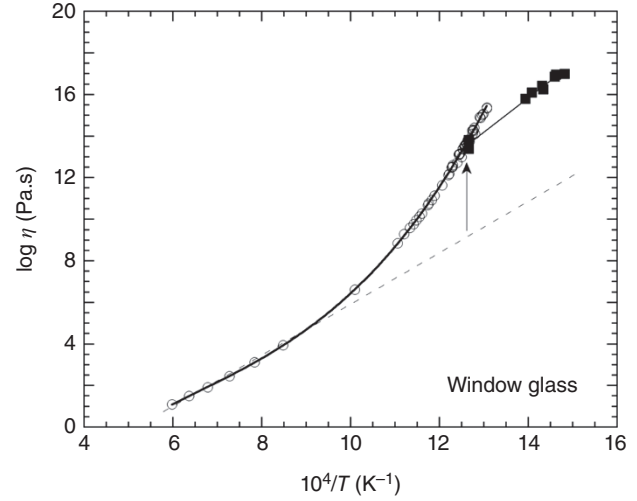


Figure 7 Viscosity of window glass; solid line VFT fit to the data; dashed line: Arrhenius fit made to the high-temperature measurements; arrow: onset of departure from the equilibrium viscosity; solid squares and line: isostructural viscosities. Source: Data from [26, 27].

$$\tau_Y = -(Y_t - Y_e) / (\partial Y / \partial t), \quad (1)$$

where Y_t is the value actually measured at time t . If τ_Y were constant, the relaxation would be exponential:

$$(Y_t - Y_e) = (Y_0 - Y_e) \exp(-t/\tau_Y), \quad (2)$$

where Y_0 is the initial Y value, so that after a time τ_Y , the variation of Y would be a fraction $1/e$ of the initial departure from the equilibrium value. Regardless of the actual non-exponential nature of relaxation, measurements, for example, made on window glass at 777 K point to relaxation times much higher than one hour (Figure 6b). A measurement performed in only a few minutes would thus refer to a fixed configuration, i.e. to a glass. Depending on the timescale of the experiment, one observes that the nature of response is thus either liquid- or solid-like.

The glass *transition range* is that temperature interval where, depending on the timescale of the experiment performed, time-dependent observations are made. It signals the change from the liquid state, where a great many different atomic configurations are unceasingly explored, to another state where atoms become trapped in fixed positions and properties become again time independent. In statistical-mechanical jargon, this change is said to represent the loss of *ergodicity* and, thus, of internal thermodynamic equilibrium.

Experimentally, the loss of equilibrium can be readily followed by viscometry. Over an interval as wide as 10 – $10^{15.5}$ Pa·s, the viscosity of a glass-forming melt can be reproduced empirically with the Vogel–Fulcher–Tammann (VFT) equation (Chapters 4.1 and 10.11):

$$\log \eta = A + B/(T - T_1), \quad (3)$$

where A , B , and T_1 are constants (Figure 7). If only high-temperature measurements are considered, then a simpler Arrhenius equation is generally adequate, viz.

$$\log \eta = \log \eta_0 + \Delta H_\eta / RT, \quad (4)$$

where η_0 is a pre-exponential term and ΔH_η the activation enthalpy for viscous flow. Consistent with the aforementioned effects of thermal history (Figure 6b), the increasing departure of the viscosities from an Arrhenius fit made to the high-temperature data (Figure 7) indicates that, independently of any thermal-energy decrease, the structural rearrangements induced by lower temperatures progressively hinders viscous flow. The effect is still more apparent when measurements are made rapidly such that structural relaxation does not take place. Under these conditions, the *isoconfigurational* viscosity is indeed lower than the viscosity of the equilibrium supercooled liquid at the same temperature (Figure 7).

2.3 The Glass Transition

2.3.1 Standard Glass-Transition Temperature

For the experimental timescales of the order of a few minutes typical of measurements of macroscopic properties, one observes that, regardless of chemical composition, time-dependent results begin to be observed when the viscosity becomes higher than about 10^{12} Pa. For convenience and comparison purposes, one defines the *standard* glass-transition temperature, T_g , as the temperature at which the viscosity of the liquid reaches this value of 10^{12} Pa.s.

2.3.2 Volume Effects

The enhanced thermal expansion coefficient observed upon heating of a glass rod in dilatometry experiments is one of the most familiar manifestations of the glass transition (Figure 8a). The marked increase over an interval of about 50 K is rapidly followed by sample collapse because the viscosity rapidly decreases so much that the sample begins to flow under its own weight before structural relaxation is complete. As a result, the volume thermal expansion coefficient [$\alpha = 1/V (\partial V / \partial T)_P = 3/l (\partial l / \partial T)_P$] may be rigorously determined from the slope of the dilatometry curve for the glass, but not for the supercooled liquid.

In dilatometry experiments, one usually defines the glass-transition temperature as the intersection of the tangents to the lower- and higher-temperature curves. This temperature generally differs somewhat from the standard T_g simply because the glass transition depends on the particular experimental conditions of the experiment. With respect to enthalpimetry, dilatometry has the advantage of yielding absolute values of the property of interest, namely, the volume (and density). The influence of thermal history on density can thus be readily determined (which is why it was observed as early as in 1845, cf. Chapter 10.11). In contrast, the thermal expansion coefficient of glasses generally does not markedly

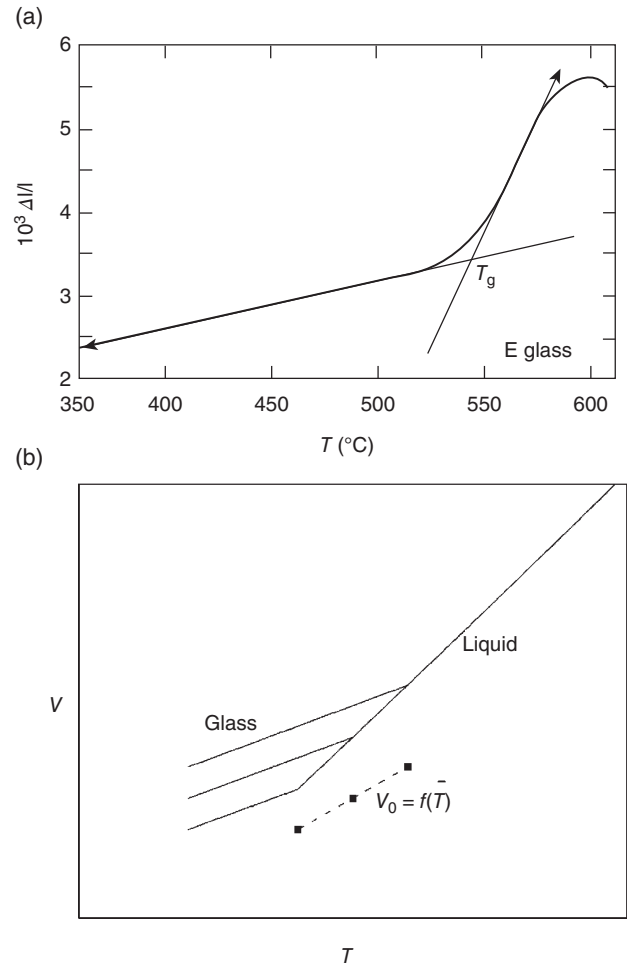


Figure 8 Volume effects of the glass transition. (a) Linear thermal expansion coefficient of E glass (Chapter 1.6) heated at 10 K/min; l = sample length (Source: Data from [28]). (b). Dependence of the volume of a glass on its fictive temperature.

depend on thermal history. At least above room temperature. The volumes of glasses produced at different cooling rates will then plot as a series of parallel lines (Figure 8b). To characterize the state of the glass, it suffices to know the temperature at which equilibrium was lost, which is directly given by the intersection of the glass and supercooled volumes (Figure 8b). This parameter is called the *fictive temperature* ($\bar{T}$), which thus represents the temperature at which the configuration of the glass would be that of the equilibrium liquid (Chapter 10.11). Knowing $\bar{T}$, it is then straightforward to determine the glass volume as a function of the fictive temperature, for example, at room temperature (Figure 8b).

2.3.3 Frequency Dependence

For exploring further the kinetics of the glass transition, one can vary the experimental timescale not only through

changes of the heating rate for a given technique, but through changes of the technique itself. In view of their relative simplicity, acoustic measurements of the adiabatic compressibility are especially interesting in this respect. For an isotropic solid, this compressibility is related to the velocities of compressional (v_p) and transverse (v_s) acoustic waves by:

$$\beta_S = 1/[\rho(v_p^2 - 4/3v_s^2)], \quad (5)$$

where ρ is the density. In a liquid of low viscosity, the attenuation of compressional waves is so rapid that one can usually consider that these waves do not propagate at all, in which case the compressibility reduces to

$$\beta_S = 1/\rho v_p^2. \quad (6)$$

Acoustic measurements are typically made with transducers working at MHz frequencies. Under these conditions, the response of the material to the compression exerted adiabatically by the acoustic waves is probed at timescales of the order of 10^{-6} seconds. To be induced by an acoustic wave, configurational changes must thus take place at timescales at least 10^6 – 10^7 shorter than those of dilatometry or calorimetry experiments. Their onset is thus correlatively observed at much higher temperatures. For a sodium silicate (Figure 9a), they are revealed above 700°C by a temperature interval where

v_p decreases markedly and becomes frequency-dependent. With respect to dilatometry or calorimetry experiments, the glass transition shifts from about 500 to 900°C , with a difference of about 50° between the measurements made at 1 and 5.6 MHz. At higher temperatures, equilibrium values of the compressibility are finally measured near 1100°C when the ultrasonic velocity becomes independent of frequency.

Experiments can be made at even shorter timescales when hypersonic sound velocities are measured by Brillouin inelastic scattering of photons by phonons (Chapter 2.2). At the timescales of the order of 10^{-10} seconds of these interactions, the glass transition shifts to higher still temperatures. For calcium aluminosilicates (Figure 9b), relaxed compressional velocities are typically observed only above 2200°C [30] where they begin to match the values determined by ultrasonic methods (Figure 9b). The first effect noticed when the temperature is increased is a slight kink (at around 750°C in Figure 9b), which disappears if the velocities are plotted against the volume of the sample instead of its temperature. This kink thus signals the increase in thermal expansion at the volume glass transition, whereas structural relaxation at the extremely short timescale of Brillouin scattering experiments becomes significant only at much higher temperatures. Interestingly, the shear sound velocities can then be measured for the supercooled liquid

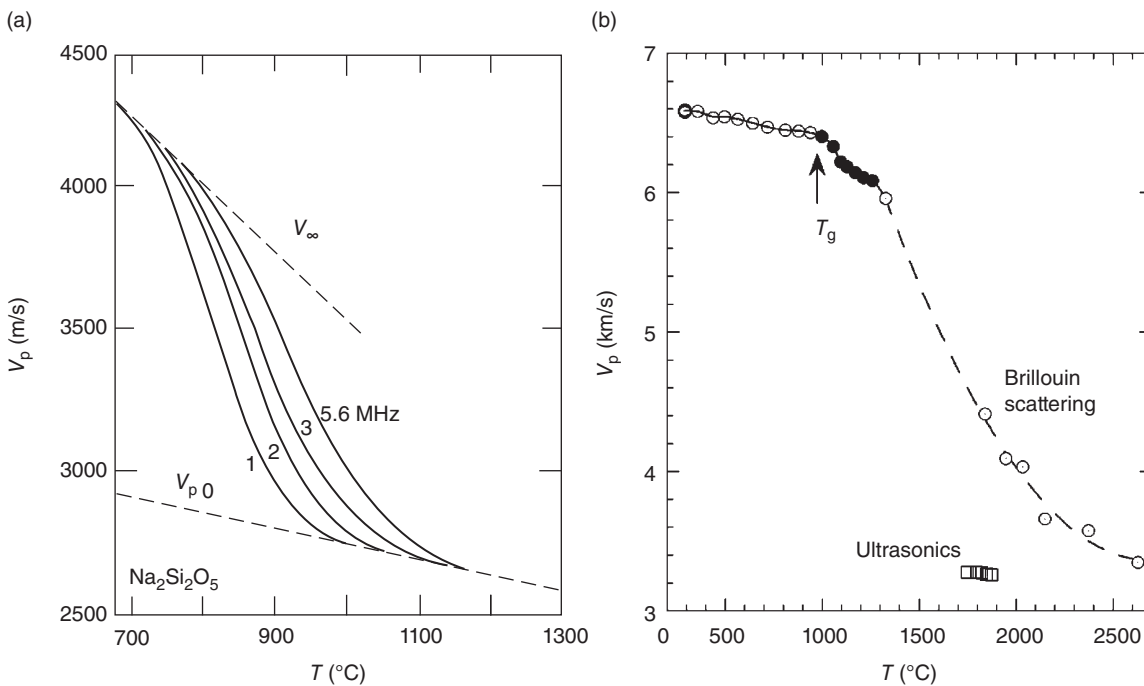


Figure 9 Frequency dependence of the glass transition range. (a) Compressional acoustic-wave velocities of sodium disilicate measured at the frequencies (MHz) indicated (Source: Data from [29]); larger width of the glass transition range than in dilatometry because of the actual distribution of relaxation times. (b) Compressional hypersonic sound velocities measured for $36 \text{ SiO}_2 \cdot 16 \text{ Al}_2\text{O}_3 \cdot 48 \text{ CaO}$ melt (mol %) by Brillouin scattering and ultrasonic methods. Source: Data from [30, 31].

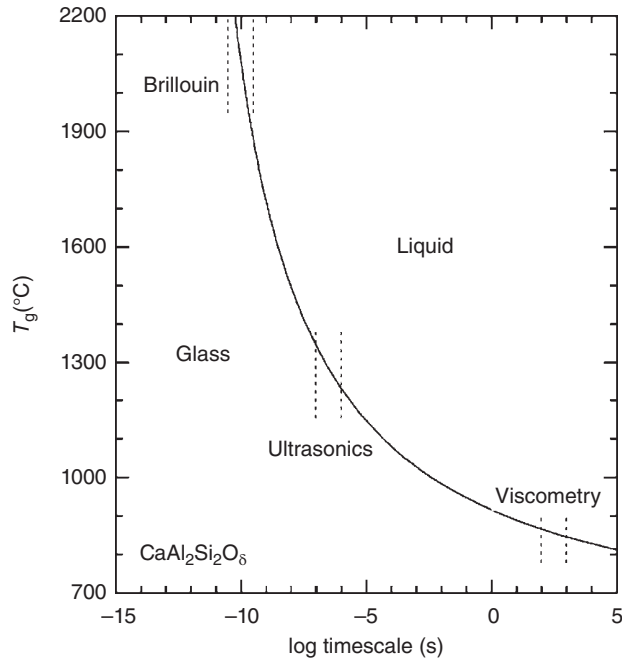


Figure 10 Time dependence of the boundary between the glass and liquid phases of $\text{CaAl}_2\text{Si}_2\text{O}_8$. Source: Data from [32].

well above the standard glass-transition temperature as long as its viscosity is not too low [32]. The material is not really a “glass” because its configuration changes rapidly with temperature, but a “glass-like” material whose solid-like part of its acoustic properties may be probed. Finally, another noteworthy feature of the glass transition range is its markedly increasing width apparent from Figures 8b to 9a and b, which originates in the fact that a distribution of relaxation times, and not a single time, must be considered. Complete relaxation is thus controlled by the slowest mechanisms whose retarding effects are the greatest for the shortest experimental timescales.

In conclusion, the question as to whether a given substance is a liquid or a glass cannot be answered if the observational timescale is not specified. One must consider instead that the transition between the two kinds of phases is represented by a curve in the timescale–temperature plane (Figure 10). The picture is actually still more complex because the glass transition also depends on pressure. With the exception of some open 3-D network structures, T_g generally increases with pressure because an increasing compaction makes configurational rearrangements more difficult. At constant timescale, the glass transition is thus represented by another curve in the pressure–temperature plane (Figure 11). And the description is still more complex if the effects of composition are also considered. If all factors are dealt with together, the glass transition then becomes a

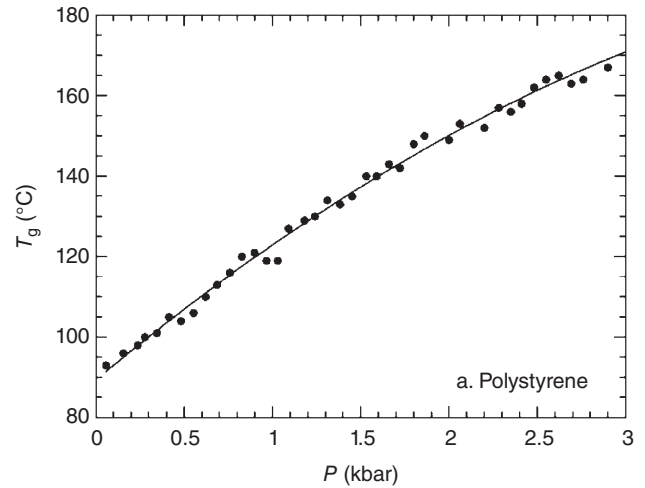


Figure 11 Pressure dependence of the glass transition of atactic polystyrene. Source: Zero-frequency Brillouin scattering data from [33].

hypersurface in the pressure–temperature–composition–timescale space.

2.3.4 An Irreversible Transition

The glass transition was first signaled by anomalous increases of the heat capacity, and its kinetic nature by the dependence of these anomalies on the thermal histories of the samples investigated (Chapter 10.11). Such effects are clearly apparent in early C_p measurements made on B_2O_3 (Figure 12a) where three different temperature intervals are distinguished [34]. Above about 270 °C, the liquid phase is in internal thermodynamic equilibrium because its heat capacity is uniquely defined by temperature (and pressure). In the 270–100 °C interval, internal equilibrium is lost as C_p is no longer defined by temperature only. The measurements made upon heating and cooling differ and C_p differences of up to 20% are found between samples initially cooled rapidly and slowly. Also noteworthy is the fact that the observed C_p hysteresis prevents a reversible thermodynamic pathway from being followed. It points instead to the creation of entropy through cycling in this interval and, therefore, demonstrates the irreversibility of the glass–liquid transformation.

Below 100 °C, C_p depends again only on temperature. If integrated from 270 to 100 °C, however, the C_p and C_p/T differences between the rapidly and slowly cooled samples represent enthalpy and entropy differences, respectively. These are constant below 100 °C as the glass C_p does not depend sensitively on thermal history. They can be readily calculated for any two glasses, like a volume difference, if their fictive temperatures are known (Chapter 3.6). An important conclusion then follows: the existence of an entropy difference at 0 K between

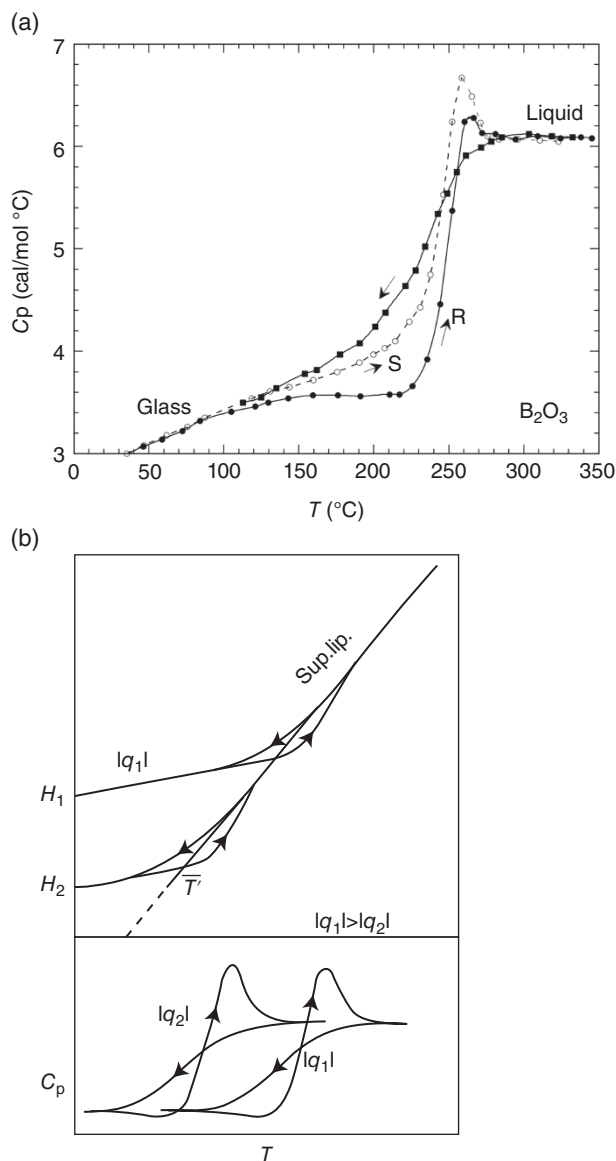


Figure 12 Irreversibility of the glass transition: heat capacity hysteresis measured for boron oxide upon cooling and upon heating of a slowly (S) and rapidly (R) cooled glass [34]. (b) Enthalpy and C_p differences between glasses cooled at different rates q ; Sup. liq.: enthalpy of the equilibrium supercooled liquid.

two samples implies that glasses have a residual entropy at 0 K: hence, glasses do not obey the third Law of thermodynamics because of the irreversible nature of the glass transition (cf. Chapters 3.6 and 10.11).

In more detail, the C_p hysteresis results from the observed contrast between a smooth decrease upon cooling and sharp increases upon heating followed by overshoots right at the end of the transition (Figure 12a). The former decrease simply points to the progressive loss of atomic mobility with decreasing temperatures. Upon

heating, the situation is more complicated because relaxation resumes at the temperature at which it vanished on cooling, but its first effect is to lower the enthalpy of the glass to bring it closer to the equilibrium values of the supercooled liquid (Figure 12b). At higher temperatures, the enthalpy curve of the material has already crossed that of the supercooled liquid when relaxation becomes almost complete at the timescale of the experiment. The heat capacity then increases rapidly (Figure 12b) in a way that depends on thermal history. The rise is highest for samples initially cooled down at the slowest rates, whose enthalpy is initially the lowest, or for samples heated at the highest rates. If the heating and cooling rates are increased, the transition shifts to higher temperatures because the decrease of the experimental timescale must be matched by an analogous decrease of the relaxation time (Figure 12b).

Determination of a glass-transition temperature is more complicated in calorimetry than in dilatometry because of the complex shapes of the observed C_p variations or even of the endothermic peaks recorded in thermal analysis. This temperature may, for instance, be taken as the inflection point of the C_p increase upon heating, but it can alternatively be defined in different ways so that is generally needed to specify which particular one has been selected [35].

2.3.5 The Case of Plastic Crystals

This description of the glass transition applies to a variety of kinetically controlled processes in crystals. *Plastic crystals*, characterized by low entropy of fusion and an unusually high plasticity, are good examples of disordered systems with three-dimensional long-range order. When the high-temperature form of cyclohexanol (ChI), for instance, crystallizes at 299 K, the $C_6H_{12}O$ molecules order in a face-centered cubic lattice but their regular shape allows them to maintain orientational mobility by rotations around the lattice points. It is through a transition to the low-temperature polymorph (ChII), which is stable below 265 K, that this dynamics vanishes and the orientational disorder disappears [36]. With rapid cooling rates, the ChI form can be obtained metastably and kept for long periods of time below 180 K. On further cooling, a transition is eventually observed near 160 K (Figure 13). The orientational disorder of $C_6H_{12}O$ molecules is then frozen in within the crystal. In contrast to the ChII form, whose entropy is zero at 0 K, ChI has a residual entropy of 4.7 J/mol K. The similarity with the glass transition phenomenology is such that the name of *glassy crystals* has been proposed for crystals where rotation of molecular groups is freed above a glass-like transition temperature and gives rise to relaxation

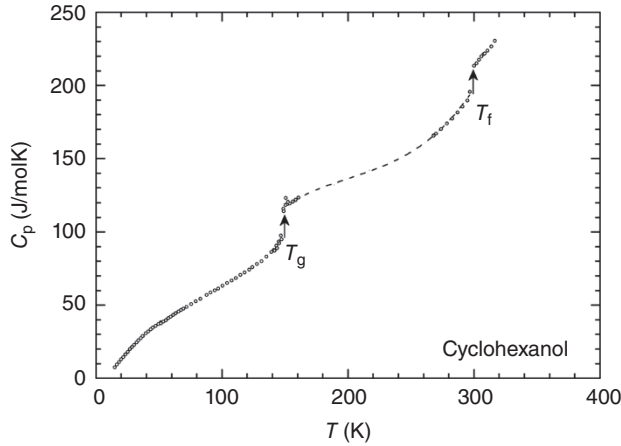


Figure 13 The calorimetric signature of orientational disorder in cyclohexanol plastic crystal. Measurements made upon heating with a gap from slightly above the glass-transition temperature T_g and the melting temperature T_f because of rapid transformation into the stable, ordered polymorph. Source: Data from [36].

phenomena much more complex than summarized here (Chapter 8.6).

2.3.6 Maxwell Model

In view of the continuous pathway between the liquid and glass states, glass-forming liquids cannot be purely Newtonian when they approach the glass transition. In fact, they are *viscoelastic*, with an elastic component that becomes increasingly important near T_g . More precisely, application of a shear stress first causes an elastic strain, which would be recovered if the stress were released, and then a viscous deformation. The response of a viscous melt subjected to stress thus is made up of an instantaneous, elastic response along with a delayed response. By combining the simplest representations of elasticity and viscous flow, Maxwell model has as a mechanical analogue a spring and a dash pot placed in series [37]. Its important result is that, if stresses are applied at low frequencies, as usually the case in viscometry, then a simple relationship holds between the viscosity, relaxation time, and shear modulus at infinite frequency (G_∞),

$$\eta = G_\infty \tau. \quad (7)$$

The fact that the glass transition is observed at values close to 10^{12} Pa.s for widely different kinds of liquids thus indicate that G_∞ also weakly depends on composition, with a mean value of about 10 GPa, which varies by less than a factor of 10 with either temperature or composition at least for oxide glass-forming liquids [38, 39]. Compared with the tremendous variations of viscosity with temperature and composition, G_∞ thus is almost constant. If the viscosity is known, structural relaxation times can be readily estimated from Eq. (7).

2.4 Configurational Properties

2.4.1 Equivalence of Relaxation Kinetics

It is usually more difficult to account for the kinetics of a reaction than for its thermodynamics. Relaxation in glass-forming systems does not depart from this rule. Whereas a single-order parameter such as the fictive temperature may be appropriate for characterizing the volume or enthalpy of a glass, relaxation kinetics requires models much too complex to be discussed here (see Chapter 3.7). One can nonetheless have a first look at the mechanisms involved in relaxation by examining whether their kinetics varies or not with the particular property considered.

As done for viscosity, the kinetics of volume equilibration can, for instance, be measured by isothermal dilatometry experiments. If samples with the same thermal history are studied, comparisons between the relaxation kinetics of different properties can be made in terms of normalized variables

$$Y = (Y_t - Y_\infty)/(Y_0 - Y_\infty), \quad (8)$$

where Y_t , Y_∞ , and Y_0 are the property Y at time t , initial time, and equilibrium, respectively. To within experimental errors, experiments on E glass, for example, show in this way the same kinetics for viscosity and volume (Figure 14).

More general conclusions are readily derived from comparison between different glass-transition temperatures even though these are not necessarily defined in the same way in different kinds of measurements. What is important is that they be defined consistently and refer to samples with the same thermal histories. For volume

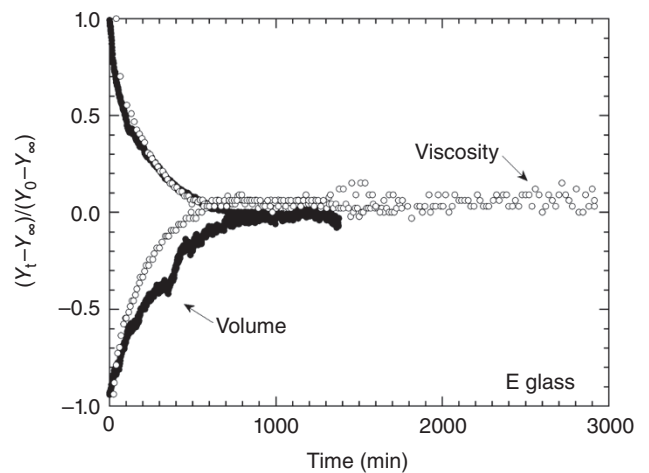


Figure 14 Kinetics of equilibration for the viscosity and volume of E glass. Differences between the ascending branches mainly due to the uncertainties on the Y_0 values caused by unrecorded relaxation during the initial thermal equilibration of the sample. Source: Data from [28].

and enthalpy, the latter condition is fulfilled in dilatometry experiments and differential thermal analyses performed simultaneously, whose results can also be compared with standard glass-transition temperatures (Figure 15). The close 1 : 1 correspondences found in this way for the three temperatures of silicates, calcium aluminosilicates, titanosilicates, and borosilicates over a 400 K

interval thus confirm the equivalence of the relaxation kinetics for differing properties [28]. In other words, one must conclude that the same configurational changes are involved in enthalpy, volume, or viscosity relaxation at least in oxide systems, which illustrates their overall cooperative nature.

2.4.2 Vibrational vs. Configurational Relaxation

The equivalence of relaxation kinetics allows an important distinction to be made between vibrational and configurational contributions to the properties of glass-forming liquids. In preamble, one should note that relaxation in solids does not need to be specifically addressed, as long as macroscopic properties are concerned, because it takes place at the 10^{-14} – 10^{-12} seconds timescale of atomic vibrations. This instantaneous vibrational response persists in liquids where it combines with the configurational response whose timescale markedly decreases with increasing temperatures (Figure 16). For volume, isothermal dilatometry experiments near the glass transition may yield these two contributions (Figure 17) whose relative magnitudes directly reflect the increase in thermal expansion at the glass transition [40]. For the compressibility, another approach may take advantage of experiments made at different timescales. As described above, in certain temperature ranges, ultrasonic measurements yield the equilibrium adiabatic compressibility whereas Brillouin scattering experiments probe only its vibrational part. The configurational compressibility is then given by the difference between these two results [32]. That such determinations are actually scarce is not too problematic for second-order thermodynamic properties because, at least as a first approximation, one can assume that the vibrational contribution is represented by the glass property and the configurational one by the variations of these

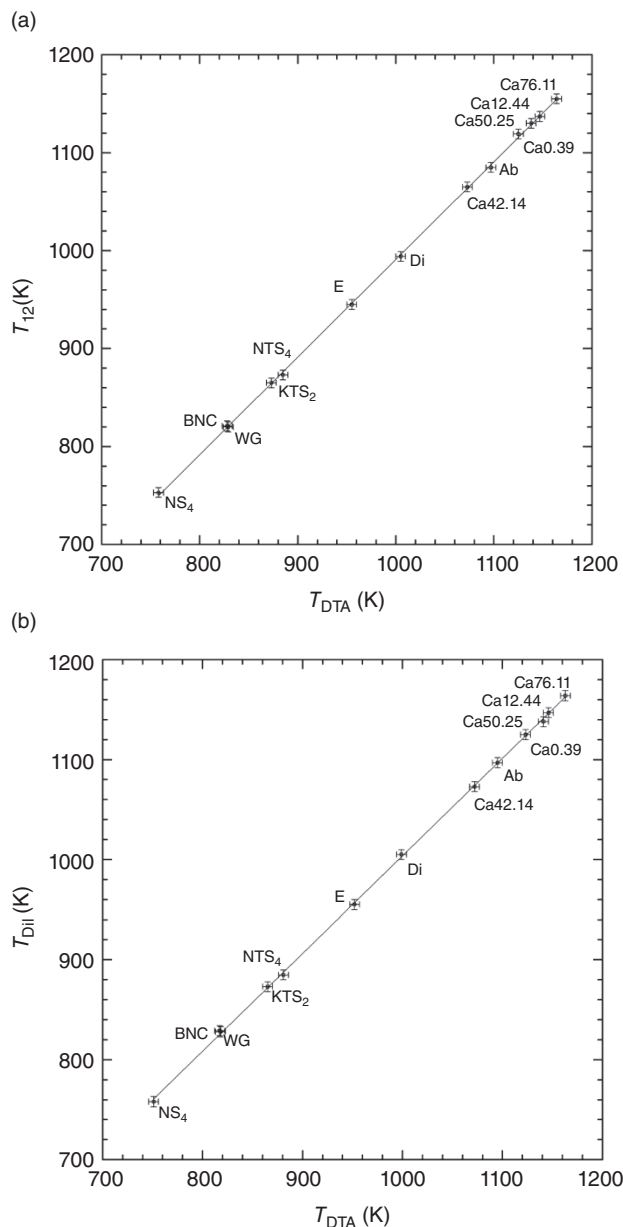


Figure 15 Equivalence of the relaxation kinetics for the enthalpy, volume, and viscosity illustrated by 1 : 1 correlations between the relevant glass-transition temperatures determined by differential thermal analysis (DTA), dilatometry (dil), and viscometry (vis, i.e. standard T_g). BNC: sodium borosilicate; WG: window glass; E: E glass; Ab: $\text{NaAlSi}_3\text{O}_8$; Di: $\text{CaMgSi}_2\text{O}_6$; N: Na_2O ; S: SiO_2 ; T: TiO_2 ; Ca.xx.yy: xx mol % SiO_2 , yy % Al_2O_3 . Source: Data from [28].

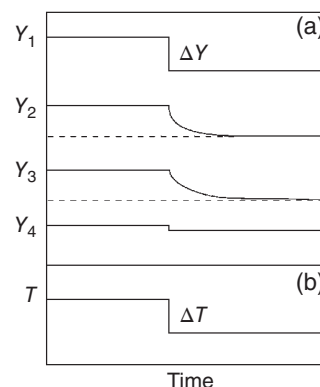


Figure 16 Relative importance of configurational and vibrational relaxation with increasing temperatures for a given property Y (a) after instantaneous temperature jumps ΔT (b). Source: Data from [40].

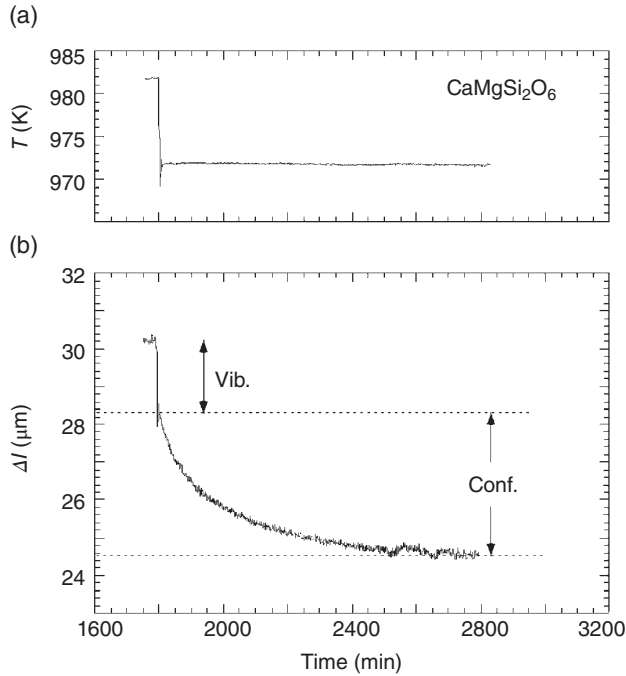


Figure 17 Vibrational and configurational contributions to the volume change of $\text{CaMgSi}_2\text{O}_6$ liquid after an abrupt temperature decrease from 982 to 972 K. Source: Data from [40], cf. Chapter 3.5.

properties at the glass transition. In silicate systems, the configurational heat capacity can thus be written

$$C_{\text{pl}}^{\text{conf}}(T) = C_{\text{pl}} - C_{\text{pg}}(T_{\text{g}}), \quad (9)$$

where the subscripts l and g refer to the liquid and glass phases, respectively, and a further simplification arises from the fact that $C_{\text{pg}}(T_{\text{g}})$ may be considered to be the Dulong–Petit harmonic limit of $3R/\text{g atom}$ (R = gas constant) the isochoric heat capacity [41].

2.4.3 A Microscopic Picture

The vibrational/configurational split can be simply illustrated by a schematic one-dimensional representation of interatomic potentials (Figure 18). Contrary to crystals, where these potentials have a long-range symmetry, glasses have essentially a short-range order because the bond angles and distances between next-nearest neighbor atoms are not constant but spread over a range of values. The minima of potential energy, which determine the glass configuration, are separated by barriers with varying heights and shapes [43]. When thermal energy is delivered to the glass, the subsequent temperature rise is associated only with increasing amplitudes of vibration of atoms within their potential energy wells. Like for any solid, the heat capacity of the glass is, therefore, only vibrational in nature.

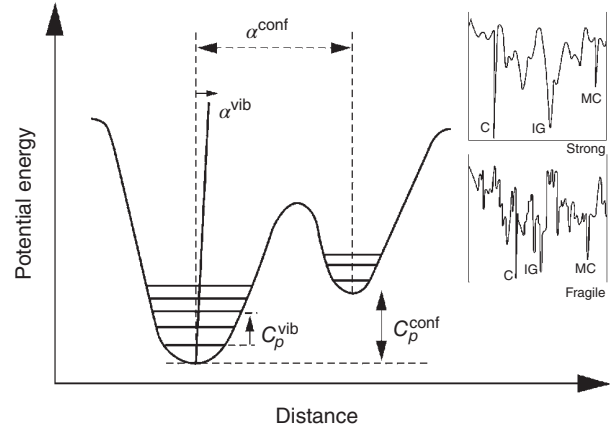


Figure 18 One-dimensional schematic representation of interatomic potentials. Inset: potential-energy landscape for a strong and a fragile liquid (Source: After [42]). C: crystal; IG: ideal glass; MC: metastable crystal.

At sufficiently high temperature, thermal energy increases to the point that atoms can overcome the barriers that separate their own from the neighboring potential energy wells (Figure 18). This onset of atomic mobility signals structural relaxation. If the relaxation time is longer than the experimental timescale, however, only the vibrational heat capacity is measured. If the temperature is increased further, or if time is sufficient for the new equilibrium configuration to be attained during the measurement, then the configurational heat capacity is also measured. When integrated over all atoms, the configurational heat capacity represents the energy differences between the minima of the potential energy wells that are explored as temperature increases (Figure 18).

The glass transition can thus be viewed as the point from which atoms begin to explore positions characterized by higher potential energies. Regardless of the complexity of this process at a microscopic level, this spreading of configurations over states of higher and higher potential energy is the main feature of atomic mobility. As a consequence, configurational heat capacities are positive. This feature, in turn, is consistent with the fact that any configurational change must cause an entropy rise when the temperature increases as required by Le Chatelier principle. As for relaxation times, they decrease with rising temperatures because large thermal energies allow potential energy barriers to be overcome more easily.

Another general feature of interatomic potentials is their anharmonic nature: displacements of the vibrating atoms from their equilibrium positions are not strictly proportional to the forces exerted on them. Because increasing vibrational amplitudes result in increasing interatomic distances (Figure 18), the thermal expansion

coefficient is generally positive for glasses. In the liquid, it increases markedly when even greater interatomic distances result from configurational changes.

2.4.4 Compressibility and Permanent Compaction

An important difference between crystals and liquids concerns the effects of pressure on their structures. The former are stable as long as the variations in their bond angles and distances induced remain consistent with their long-range symmetry. A transition to a new phase takes place when this constraint is no longer respected. In contrast, the lack of long-range order makes a wide diversity of densification mechanisms possible in a liquid, whose structure thus keeps constantly adjusting to varying pressures through changes in short-range order characterized by shorter equilibrium distances and steeper slopes around the minima pictured in Figure 18. The compressibility is thus greater for a liquid than for its isochemical crystal. It is also made up of vibrational and configurational contributions. Because the shape of interatomic potentials determines the vibrational energy levels, compression is termed vibrational for the elastic part of the deformation. As for the configurational contribution, it is related to the aforementioned changes in the potential energy wells.

If a liquid is quenched as a glass at high pressure, the final glass recovered after decompression will be denser than its counterpart formed at room pressure because only the vibrational part of the compression is eventually recovered (Figure 19). But permanent densification can also be achieved at room temperature through compression of a glass at a few tens of kbar (Chapter 10.11). The effects of pressure and temperature on the properties of glasses are thus of a different nature since the kinetics

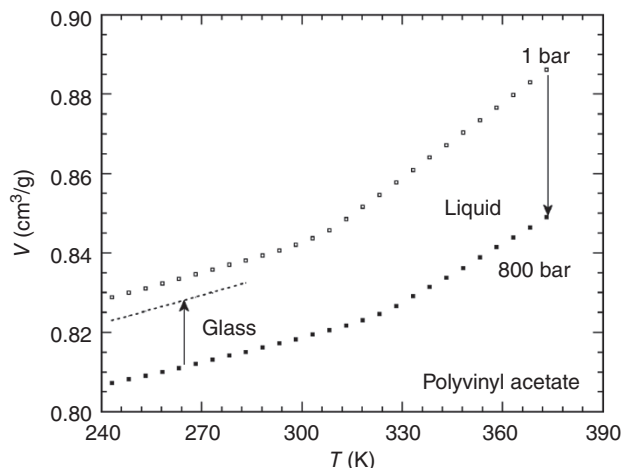


Figure 19 Permanent compaction of polyvinyl acetate after compression at 800 bar (80 MPa) in the liquid state. Source: Data from [44].

of pressure- and temperature-induced configurational modifications are markedly different for given frequencies or experimental timescales. This dissimilarity mainly originates in the fact that the shape of potential energy wells varies little with temperature, but significantly with pressure. If a high kinetic energy is needed to overcome potential barriers at constant pressure, the changes in these barriers with pressure can lead by themselves to new configurational states, at low temperatures, if the pressure is high enough.

2.4.5 Kauzmann Paradox

When viscous liquids escape crystallization, why do they eventually vitrify instead of remaining in the supercooled liquid state? One answer to this question is purely kinetic and relies only on increasingly long relaxation times on cooling. If experiments could last forever, any glass would eventually relax to the equilibrium state. Then, the glass transition would result only from the limited timescale of feasible measurements. A simple thermodynamic argument known as Kauzmann's paradox [45] indicates that this answer is incorrect. At its basis is the existence of a configurational contribution that causes the heat capacity of a supercooled liquid to be generally higher than that of an isochemical crystal and its entropy to decrease faster than that of a crystal when the temperature is lowered (Figure 20). If the entropy is extrapolated to temperatures

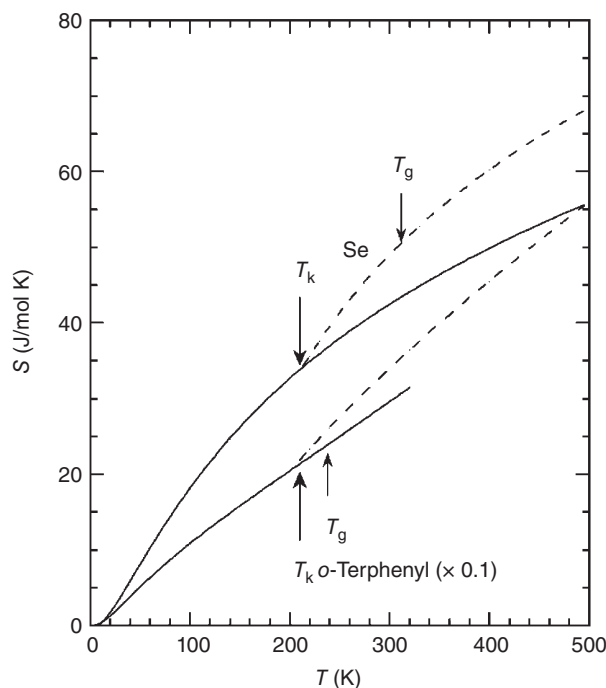


Figure 20 Kauzmann catastrophe for amorphous selenium and ortho-terphenyl (C_8H_{14}). Differences between the glass transition and Kauzmann temperatures indicating the smallness of the C_p extrapolations performed. Source: Data from [46, 47].

below the glass transition range, it becomes lower than that of the crystal at a temperature T_K , which is high enough for such an extrapolation to remain reasonable. Although this situation is not thermodynamically forbidden, it seems unlikely that an amorphous phase could have a lower entropy than an isochemical crystal.

The conclusion is that an amorphous phase cannot exist below T_K . The temperature of such an entropy catastrophe constitutes the lower bound to the metastability limit of the supercooled liquid. As internal equilibrium cannot be reached below T_K , the liquid must undergo a phase transition before reaching it. This is, of course, the glass transition. In its original form, Kauzmann's paradox implicitly neglects possible differences in vibrational entropy between the amorphous and crystalline phases. This simplification is actually incorrect but it does not detract from the gist of the argument, for taking into account such differences would only shift T_K slightly. A more rigorous statement of the paradox is that the catastrophe would occur when the configurational entropy of the supercooled liquid vanishes.

2.4.6 Potential Energy Landscape: Ideal Glass and Fragility

Among the great many statistical mechanical models that have attempted to account for the glass transition and solve Kauzmann's paradox, the early one proposed by Gibbs and Di Marzio [48] is of special interest. It predicts that the supercooled liquid would transform to an *ideal* glass through a second-order transition at the temperature T_0 at which its configurational entropy would vanish. Since then, the existence and the nature of such a transformation have been much debated. This debate notwithstanding, the important point for our discussion is the result subsequently derived by Adam and Gibbs [49] on the basis of a lattice model of polymers. This result is a very simple relationship between relaxation times and the configurational entropy of the melt, viz.

$$\tau = A_e \exp(B_e/TS^{\text{conf}}), \quad (10)$$

where A_e is a pre-exponential term and B_e is approximately a constant proportional to the Gibbs free energy barriers hindering the cooperative rearrangements of the structure.

Qualitatively, this theory assumes that structural rearrangements would be impossible in a liquid with zero configurational entropy so that relaxation time would be infinite. If two configurations only were available for an entire liquid volume, mass transfer would require a simultaneous displacement of all structural entities. The probability for such a cooperative event would be extremely small, but not zero, and the relaxation times would be extremely high, but no longer infinite. When

configurational entropy increases, the cooperative rearrangements of the structure required for mass transfer can take place independently in smaller and smaller regions of the liquid.

Within this picture, relaxation is determined by the topology of potential energy wells in an n -dimensional space and, particularly, by the density and relative depths of these wells as may be illustrated in a 1-d representation of such a *potential-energy landscape* (Figure 18, insets).

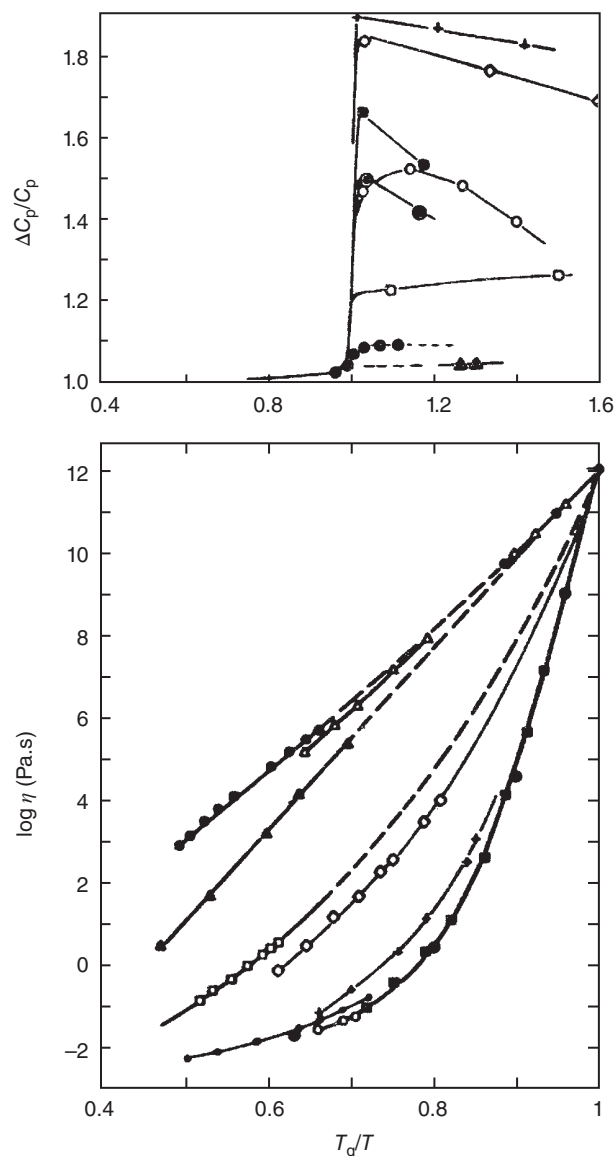


Figure 21 Fragility as a measure of the extent of temperature-induced configurational changes in inorganic and organic glass-forming liquids: correlations between relative C_p increases at the glass transition and deviations of viscosities from Arrhenius laws (Source: After [52]). Lower panel, from top to bottom: SiO_2 , GeO_2 , BeF_3 , ZnCl_3 , LiCH_3COO , $4 \text{ Ca}[(\text{NO}_3)_2] \cdot 4 \text{ H}_2\text{O}$, *o*-terphenyl, glycerol ($\text{C}_3\text{H}_8\text{O}_3$), and $\text{H}_2\text{SO}_4 \cdot 3 \text{ H}_2\text{O}$.

A simple distinction can then be made between strong and fragile liquids [43, 50]. For the former, a low density of wells translates into a small configurational heat capacity and entropy and thus, in small departures from an Arrhenian temperature-dependence of relaxation times as given by Eq. (7); for the former, the high density of wells is in contrast associated with high configurational heat capacities and entropies, and marked deviations from Arrhenian temperature dependences.

Owing to the simple proportionality between relaxation times and viscosity, this difference may be simply visualized in plots of viscosities as a function of T_g/T where T_g is the standard glass-transition temperature [51]. A well-known sketch (Figure 21) illustrates the point for a variety of inorganic and organic glass-forming liquids [52]. As particularly exemplified in Chapter 4.1, this duality between fragile and strong liquids will be a recurrent theme in many other chapters of the *Encyclopaedia* to which the reader is thus referred.

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Appendix A

Table A.1 Coordination numbers, effective ionic radii, field strengths, and electronegativities of some cations and anions of interest in oxide glasses. *Source:* Compilation courtesy J.F. Stebbins.

	Coordination ^a	Ionic radius ^b (Å)	Field strength ^b	Electronegativity ^c
<i>Anions</i>				
O ²⁻	2, 6	1.35, 1.40	—	3.5
F ¹⁻	2, 6	1.29, 1.33	—	4.0
Cl ¹⁻	6	1.81	—	3.0
<i>Cations</i>				
<i>Network formers^d</i>				
Fe ³⁺	4, 6	0.49, 0.55	0.88, 0.82	1.8
Ga ³⁺	4, 6	0.47, 0.62	0.90, 0.77	1.6
Al ³⁺	4, 6	0.39, 0.54	0.98, 0.83	1.5
Te ⁴⁺	3, 4 ^e	0.52, 0.66	1.13, 0.98	2.1
Ti ⁴⁺	4, 6	0.42, 0.61	1.26, 1.03	1.5
Ge ⁴⁺	4, 6	0.39, 0.53	1.31, 1.12	1.8
Si ⁴⁺	4, 6	0.26, 0.40	1.52, 1.29	1.8
B ³⁺	3, 4	0.01, 0.11	1.60, 1.41	2.0
P ⁵⁺	4	0.17	2.14	2.1
<i>Modifier to intermediate: alkalis and alkaline earths</i>				
Cs ¹⁺	8	1.74	0.10	0.7
Rb ¹⁺	8	1.61	0.11	0.8
K ¹⁺	8	1.51	0.12	0.8
Na ¹⁺	6	1.02	0.18	0.9
Li ¹⁺	4, 6	0.59, 0.76	0.26, 0.22	1.0
Ba ²⁺	8	1.42	0.26	0.9
Sr ²⁺	8	1.26	0.29	1.0
Ca ²⁺	6, 8	1.00, 1.12	0.36, 0.33	1.0
Mg ²⁺	4, 6	0.57, 0.72	0.53, 0.46	1.2
Be ²⁺	4	0.27	0.75	1.5
<i>Modifier to intermediate: selected others</i>				
Sn ²⁺	8 ^e	1.26	0.29	1.8
Pb ²⁺	4, 8 ^e	0.98, 1.29	0.37, 0.28	1.9
Mn ²⁺	6	0.83 ^f	0.42	1.5
Fe ²⁺	6	0.78 ^f	0.44	1.8
Zn ²⁺	4, 6	0.60, 0.74	0.52, 0.45	1.6
Ni ²⁺	4, 6	0.55, 0.69	0.55, 0.48	1.9
La ³⁺	8	1.16	0.47	1.1
Nd ³⁺	8	1.11	0.49	1.1
Er ³⁺	8	1.00	0.54	1.2
Y ³⁺	8	1.02	0.53	1.2
Sc ³⁺	6	0.75	0.67	1.3
Sb ³⁺	4 ^e	0.76	0.67	1.9
Zr ⁴⁺	8	0.84	0.83	1.4

Table A.1 (Continued)

	Coordination ^a	Ionic radius ^b (Å)	Field strength ^b	Electronegativity ^c
U ⁴⁺	6	0.89	0.79	1.7
Mo ⁶⁺	4, 6	0.41, 0.59	1.92, 1.58	1.8

^a Common coordination numbers; others may occur. Five-coordinate states are also known for many cations listed with 4 and 6 coordination (e.g. Al, Si, Ti, Ni), which have intermediate radii and field strengths.

^b Cation field strength, valence divided by square of cation–oxygen distance, with the radius of the latter taken as 1.36 Å, the typical value for three-coordinated O.

^c Pauling electronegativity, from Pauling, L. (1970). *General Chemistry*. San Francisco: W.H. Freeman.

^d “Network former” description is generally most appropriate for lower coordination numbers.

^e Lone-pair electronic structure may lead to lower coordination than expected from radius.

^f Radii for high spin electronic state.

^g Effective ionic radius, from Shannon, R.D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* A32, 751–767.

Table A.2 S.I. units and physical constants.

	Symbol	Value	Unit
<i>Universal constants</i>			
Speed of light	c	$2.999\,792\,458\,10^8$	m/s
Gravitation constant	G	$6.674\,08\,(31)\,10^{-11}$	m ³ /kg/s
Planck constant	h	$6.626070\,10^{-34}$	J/s
		$4.135669\,2\,(12)\,10^{-15}$	eV s
<i>Masses</i>			
Electron	m_e	$9.109383\,56\,(11)\,10^{-31}$	kg
Proton	m_p	$1.672621898\,(21)\,10^{-27}$	kg
Neutron	m_n	$1.674927471\,(21)\,10^{-27}$	kg
<i>Physical constants</i>			
Avogadro number	N_A	$6.022140857\,(74)\,10^{23}$	
Faraday constant	F	$9.648533212331001\,84\,10^4$	C/mol
Ideal gas constant	R	$8.3144598\,(48)$	J/mol/K
Boltzmann constant	k	$1.380649\,10^{-23}$	J/K
	k/hc	$69.503\,87\,(59)$	m ⁻¹ /K
Stefan–Boltzmann constant	σ	$5.670367\,(13)\,10^{-8}$	W/m ² /K ⁴
Molar volume of ideal gases (at 273.15 K and 1 atm)	V_m	$22.413\,962\,(13)\,10^{-3}$	m ³
<i>Conversion factors</i>			
Electron-Volt	eV	$1.6021766208\,(98)\,10^{-19}$	J
Standard atmosphere	atm	$101.325\,10^3$	Pa

Numbers in brackets denote the uncertainties in the final decimal places. Reported values by definition exact when no uncertainties are mentioned.

Section I. Glassmaking

Figure 1 The initial melting step in the making of float glass: the 1-m deep bath of raw materials melted by the flames of a cross-fired furnace (Chapter 9.7). Pulls ranging from 500 to 1000 tons/day and mean residence times of at least 24 hours. Electro-fused refractory materials made up of alumina-zirconia-silica in contact with the melt, and of alumina and alumina-silica elsewhere (cf. Chapter 9.8). *Source:* Photo courtesy Simonpietro Di Pierro, Saint-Gobain Research Paris.



Compared with crude steel (1700 million tons/year worldwide) and especially with cement (4300 Mtons), glass (about 120 Mtons) is produced in relatively small quantities. In terms of product value or volume, however, the imbalance is significantly reduced since the cost of cement is about one sixth of that of window glass and steel about three times as dense. But what differentiates glass most from these other two inorganic pillars of modern civilization is the remarkable diversity of its uses illustrated throughout the Encyclopedia.

In Europe, for which the data are the most readily available, the 35 Mtons produced in 2017 were split into container (21.4), flat (10.1), domestic (1.3), reinforcement (0.7), and other (1.1) glass. For both container and flat glass, the world market is estimated to be in the 60–80 billion \$ range and is expected to keep growing in the years to come at yearly rates higher than 5% on average, with large geographical differences (cf. Chapter 9.6). And growth rates should be higher still for new products such as the *smart* glass used in a variety of electronic devices (cf. Chapter 6.10), whose market should increase by a factor of 3 from 2017 to 2023 from the current few billion \$ per year.

Like cement and steel producers, glassmakers sell more than 90% of their production to other industries. Most uses of glass are nonetheless familiar to anyone. These are summarized in the first chapter of this section where R. Conradt points out their strong dependence on chemical composition of the glasses and on their ensuing physical properties, explaining that the reason why the still-dominant soda-lime silicates were empirically found so early in the history of glassmaking is simply because they lie close to the eutectic of the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system.

Even though glass is now made in many different ways for different applications, the traditional procedure of making it by cooling of a batch melted at high temperatures remains by far prevailing. As one readily realizes when looking at the original glazing of late-nineteenth-century buildings, the long-standing problem faced by glassmakers was to achieve chemical homogeneity. The mass production of defect-free glass is a relatively recent achievement. It has resulted from better furnaces (Figure 1; Chapters 9.7 and 9.8), higher melting temperatures, and more carefully selected raw materials. In the Chapter 1.2, S. Di Pierro thus discusses the importance of the specifications, sources, and management of raw materials needed to avoid high rejection costs after

melting operations that must be as fast as possible for economic reasons (Chapter 1.2). Being common to most glassmaking processes, fusion itself is then reviewed by R. Conradt from a dual thermodynamic and kinetic standpoint; the account includes not only the fundamental reaction and dissolution steps of the batch ingredients but also the fining and homogenization of the melt produced (Chapter 1.3).

The second part of the section is devoted to the making of three basic products. Flat glass is dealt with by T. Kamihori. He begins with the first mechanical methods devised at the turn of the nineteenth and twentieth centuries, turns to the famous float process, which revolutionized the flat-glass industry in the 1960s, and ends with the recent drawdown processes widely used to produce new glasses for electronic applications with ever stricter quality specifications (Chapter 1.4). Container glass is considered by C. Roos who briefly presents the first forming devices designed at the beginning of the twentieth century before describing the various ways in which a bottle is now shaped with *Individual Section* machines at extremely high rates and may then be protected by treatments such as coating to enhance resistance to breakage (Chapter 1.5). In the next chapter, the drawing of continuous glass fibers for the relatively small but important reinforcement market is considered by H. Li and J. Watson in terms of both processes and composition evolutions driven by the need to improve chemical and physical properties (Chapter 1.6). That computer modeling of glassmaking has become an important tool to save time and money in the design or improvements of plants is explained by P. Prescott and B. Purnode in the final chapter of this section, which shows that, in industry too, fundamental insights and an accurate knowledge of the physical properties of melts have become badly needed (Chapter 1.7).

Other processes and their products are too diverse to be gathered into a common chapter. Hence, they are described along with some of their important applications: the secondary fabrication of flat glass in Chapter 9.2, the making of thermal insulation fibers in Chapter 9.3, of sol-gel products in Chapter 8.2, of glass tubes in Chapter 7.7, and of light bulbs in Chapter 6.9. Other fabrication issues are dealt with in chapters devoted to modern furnaces (Chapters 9.7 and 9.8), cullet recycling (Chapter 9.9), and the history of glassmaking processes (Chapters 10.5, 10.7, and 10.8).

1.1

Glass Production: An Overview

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1 Introduction

The term “glass” may either refer to a special state of matter in general or to a group of industrially manufactured materials. The chart in Figure 1 presents, from a chemical point of view, an overview of a large number of systems that can be easily transferred into the glassy state. In this chart, special emphasis is given to the industrially relevant group of silicate glasses because, by volume or mass, the vast majority of the glasses produced belong to it. Nonsilicate oxide glasses and other inorganic nonmetallic glasses, nevertheless, play an essential role in the production of highly specialized functional materials such as optical fibers (Chapter 6.4). The group of “other glasses” comprises materials of very different nature. Within this group, metallic glasses (Chapter 7.11) are finding a variety of practical applications whereas organic glasses (Chapters 8.7 and 8.8) have long played a major role at the industrial scale.

No attempt is made here to present a concise definition of the glassy state in general. From a practical point of view, however, glasses comprise a group of noncrystalline homogeneous and isotropic materials characterized by the absence of any microstructure. Thus, in contrast to (poly)crystalline materials, the bulk properties of which are essentially tailored via their microstructure, those of glasses are chiefly designed via their chemical composition; by contrast, thermal treatment has a comparatively small “fine-tuning” effect, which may, nevertheless, become crucial for specific products (e.g. optical or *strong* glasses).

At the atomic scale, the very same bonding interactions are present in isochemical condensed phases, i.e. in liquids, glasses, and crystalline polymorphs. Therefore, the chemical and electronic properties of glasses resemble those of their crystalline counterparts – with the reservation that glasses typically possess larger molar volumes, higher entropies, and higher (less negative) enthalpies of formation. In other words, they are thermodynamically less stable than crystals. Nevertheless, their macroscopic properties reflect in essence the same dependences on chemical composition as their crystalline counterparts. Without mentioning a host of other polymorphs, SiO₂ may, for example, exist under ambient conditions as quartz, cristobalite, or vitreous silica; thermodynamic stability decreases in the given order. The same applies to hydrolytic stability, a macroscopic property for which all SiO₂ polymorphs nonetheless stand out by comparison with other oxides.

In general, information on atomic bond strengths, compound formation energies, and phase equilibria in a system of a given chemical composition may serve as reliable guidelines to explore the relation between the chemical composition of a glass and its macroscopic properties. It would go too far to draw the same conclusion for the relation between the chemical composition and the short-range order structure. Although there is ample experimental proof for such a relation in many systems [1], the general claim may be misleading, even erroneous in specific instances. Yet, in any case, the energetics pertaining to a specific glass structure is in general very close to that of an isochemical crystalline system. Energetics, in turn, is the key factor governing the relation between the chemical composition of a glass and its macroscopic properties. For this reason, equilibrium phase diagrams ([2, 3], Chapter 5.2) and thermochemical databases [4–9] are most helpful tools in the design of glass compositions with desired properties.

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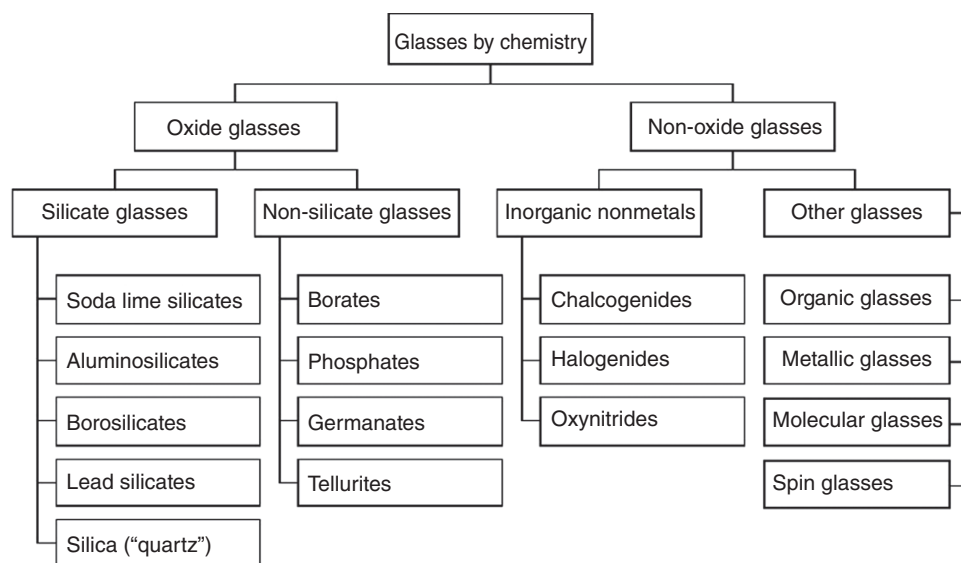


Figure 1 Glass-forming systems, classified by chemical composition.

The industrial synthesis of glasses can also be based on a large systematic collection of experimental data of the properties of glass-forming systems [10–14]. Because at a microscopic level, atomic interactions are primarily pairwise (Chapter 2.7), one can in particular make use of empirical composition–property relations [15–20] of the type

$$P = \sum a_j \cdot p_j + b_j \cdot p_j^2 + \dots, \quad (1)$$

where P denotes a macroscopic property, p_j is the mol or weight fraction of component j , and the a_j and b_j coefficients are sets of empirical parameters representing the contribution of component j to the property P of the glass.

2 Industrially Manufactured Glasses

2.1 Properties of Manufactured Glasses in General

In addition to the influence of chemical composition, it is the homogeneity, isotropy, and absence of any microstructure that brings about the main features shared by most industrially manufactured glasses. This group of materials stands out from others by

- aesthetics; historically, the fact that glass was looking like gems has been the predominant driving force for the invention of glass as a material (Chapter 10.2). Aesthetic requirements today remain an important aspect, technically expressed as *quality* since, for instance, the presence of a single blister calls for the rejection of a 3×6 m sheet of flat glass.
- its suitability for large-scale continuous primary forming as sheets, rods, tubes, and fibers.
- its extreme variability of shapes in discontinuous forming, comprising shapes with undercut.
- optical transparency. By virtue of their electronic and ionic properties, homogeneity, and absence of any microstructure, most glasses have an excellent transparency in the visible range. A standard float glass (4 mm thick) is transparent for light at wavelengths from 300 to 3500 nm, covering the entire visible (400–760 nm) and the near-IR ranges, the reflection losses of a standard glass sheet remaining slightly lower than 8%.
- an extremely wide and continuous compositional variability. Glasses can also easily incorporate functional components such as colorants.
- an extremely smooth surface, which originally allowed glass not to “smell” the odors of the substances it was storing. Today an as-received float glass possesses a roughness (root mean squared [RMS] value) of approximately 0.5 nm on the atmosphere side, and 1 nm on the tin-bath contact side. Even after an extended exposure to water or humid air at room temperature, RMS remains well below 10 nm. This makes glasses ideal substrates for metal and other functional coatings.
- excellent dielectric properties. Lead silicate glasses used in the back part of cathode-ray tubes reach dielectric constants of 20. It is true, this number does not match the extremely high values of functional ceramics (polycrystalline $\text{TiO}_2 \approx 100$, $\text{BaTiO}_3 \approx 1000$). When it comes to breakthrough voltages, however, the lack of any microstructure confers a clear advantage to glasses over polycrystalline materials: polycrystalline alumina withstands less than 8–9 kV/mm, whereas alkali-free

glasses reach 40 kV/mm, like natural mica; glass ceramics doped with BaTiO₃ crystals may even reach values higher than 400 kV/mm.

- excellent chemical durability against most chemicals. This is especially the case for silicate glasses in the low-pH range (i.e. with strong acids), making them excellent materials for chemical-process plants.
- an extremely high stiffness and intrinsic strength, both again by virtue of the absence of any microstructure. With a tensile strength of up to 4000 MPa (glass fibers), glass ranges among the strongest materials available. Its proverbial fragility is not a matter of strength, but of vulnerability of its surface and of low fracture toughness (Chapter 3.11).

It is a combination of the above features which gives glass such a prominent and indispensable place in the world of materials.

2.2 Classification of Glasses by Commercial Branches

From a technical point of view, glasses are classified in terms of applications rather than chemical composition. The following list presents the most important groups of industrial products under this aspect.

Glass hollowware

Container glass	Bottles (flint, green, amber) Preserving jars Flaconnage
Tableware	Stemware, kitchenware, vases

Flat glass

Architectural glass
Glass for personal security and property protection
Glass for photovoltaic application
Fire-resistant glass
Automotive glass
Decorative interior glass and mirrors

Fiber glass

Continuous fibers (textile; reinforcement)	Multi-purpose (E) Acid resistant (A, C, E-CR) Alkali resistant (AR) High strength (R, S) Dielectric (D)
Fibers for thermal and acoustic insulation	Glasswool, stonewool

Other glass, comprising specialty glass

Soluble glass (water glass)	For chemicals and detergents
Foam glass	For thermal insulation
Laboratory and industry	Lab ware glasses Glasses for process plants Electrode glasses
Artificial lighting	Incandescent lamps Gas-discharge lamps Semiconductor light sources Reflectors
Pharmaceutics and medicine	Ampoules and vials Antibacterial glasses Bioactive glasses
Optics	Eyeglasses Cameras, microscopes, telescopes Fiber optics and endoscopy Telecommunication fibers Laser glasses
Electronics and energy generation	Electronic tubes Sealing glasses Soldering and passivation glasses Substrate glasses and display glasses Glasses for thermal power generation
Radiation protection	Radiation shielding windows High-energy radiation detection windows
Silica ("quartz") glass	For high-T processing For silicon crystal growth For silicon-wafer handling For optical fibers

The pie chart in Figure 2 provides a rough overview of the shares of these categories by amounts of worldwide production. The figures given are estimates based on an evaluation of multiple sources for the time span 2003–2008. By absolute amounts, the 2005 world production reached about 124 million metric tons (31 in the European Union, 8 in Germany). Since then, an average annual increase of about 3.5% is observed. Whereas the production is more or less leveling off in most industrialized countries, the PR of China is among the main

driving markets for this increase as its 2005 output of flat glass already accounted for more than 50% of the world production (cf. Chapter 9.6).

For each type of glass products listed above, a typical chemical composition range has been adopted world-wide. The compositions of container and flat glass have never been developed by a scientific approach. Rather, they have remained pretty the same ever since the beginnings of glass makings (Chapter 10.2). Compositions have thus been very early constrained by the availability of affordable raw materials, the need to prevent water corrosion, and the highest temperatures reached in furnaces.

A systematic scientific approach to glass compositions did not begin before the nineteenth century, chiefly promoted by the work of individuals such as Fraunhofer,

Faraday, Harcourt, Abbé, or Schott (Chapter 10.11). Since then, this scientific approach has remained the basis for designing not only the compositions of most specialty glasses but also to improve those of existing products. For example, there is a quest among the producers of continuous fibers for completely new compositions with outstanding mechanical or chemical properties such as high modulus for lightweight construction composites or extreme alkali resistance for concrete reinforcement. In other cases, the driving force for development stems from environmental or health concerns and legislation. As examples, lead and arsenic oxides are being replaced in the formulae of optical glasses, solder and sealant glasses, and even in crystal tableware, whereas insulation-fiber compositions have been reformulated to avoid any confusion with asbestos fibers whose cancerogenic potency is well known. The typical composition ranges of current glass products are summarized in Table 1.

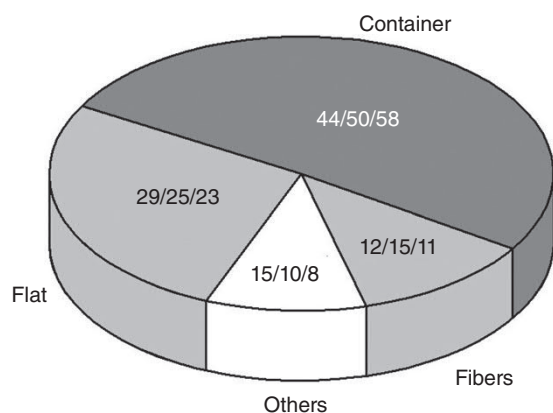


Figure 2 Glass production by branches; figures in % in the sequence world/United States/Europe.

3 Process-controlling Properties

3.1 Viscosity

Among all the properties of a glass-forming substance, the viscosity–temperature relationship is by far the most important practically in glass making. Referring to Chapter 4.1 for an in-depth review of this topic, here we will consider it from a simpler technological point of view. The main feature then is that the viscosity of a glass-forming liquid extends over a range of 12–14 orders of magnitude, which thus involves large rheology changes in the temperature range relevant to glass manufacturing

Table 1 Typical compositions of industrial glasses comprising main oxides only (no colorants or impurities); compositional ranges from multiple sources (e.g. [13]) or typical individual examples (wt %).

Oxide	Container glass	Float glass	Crystal glass	Display glass	E fiber glass	Glass wool	Stonewool	Low- α glass	Soluble glass
SiO ₂	66–75	70–74	66.0	65.0	52–60	56–66	35–48	70–81	66–77
TiO ₂			1.0				0–3		
Al ₂ O ₃	1–3	0.5–1.5	2.0	18.0	12–16	0–6	12–28	2.5–5	
Fe ₂ O ₃							3–12		
B ₂ O ₃				1.0	0–9	3–9		10–15	
MgO	0–4	0–4	4.0	7.0	0.5–4.5	1–5	2–11	1.0	
CaO	8–12	7–10	6.0	6.0	16–24	5–11	10–28	1.0	
BaO			2.0	3.0					
ZnO			3.0						
Li ₂ O	0–1							0–1	
Na ₂ O	11–15	12–14	8.0		0–2	13–17	1–6	4–8	23–34
K ₂ O	0–2	0–1				0–2	1–6	0–3	

Table 2 Viscosity ranges of industrially manufactured glasses.

Viscosity as log η , η in dPa·s	Process range, technological meaning ^a
Melting	
2.0	Typical of a soda-lime silicate glass melt at 1450 °C
3.0	Transfer to forming area Volume relaxation time is <1 s Fixpoint $T(3.0)$ = gob temperature Bushing tip temperature for fiber production ^b
Forming	
4.0.	Upper limit of mechanical working range Fixpoint $T_{WP} = T(4.0)$ = working point
6.0	Lower limit of mechanical working range The difference $T(4.0) - T(6.0)$ is termed the “length” of a glass
Tempering, annealing, and cooling	
7.6	Upper limit of macroscopic shape stability Fixpoint $T_L = T(7.6)$ = Littleton softening point
11.0 ^c	Dilatometric softening point T_D Above T_D , temperature gradients in a glass object no longer cause thermal stresses A related temperature level is $T_d = T(11.5)$ = deformation point Glass objects deform under own weight at rates of a few $\mu\text{m/h}$
13.0	Technical definition of the glass transition Fixpoint $T_g = T(13.0)$ = annealing point Volume strain relaxation time is 60 s
14.5	Technical definition of ultimate transition to a rigid state Fixpoint $T(14.5)$ = strain point Volume strain relaxation time is 30 min

^a In the earlier days of mechanical forming, empirical indicators were in use. They remain worth to be consulted as empirical guidelines when the complex feature of “workability” is to be kept constant under a compositional change; these indicators read: gob temperature, $GT = 2.63 \cdot (T_L - T_g) + T_L$; working range index $WRI = T_L - T_g$; RMS = relative machine speed = $(T_L - 450)/(WRI + 80)$; DI = devitrification index = $WRI - 160$.

^b Some stonewool processes use $T(1.5)$ as fibrization temperature.

^c Approximation, the exact value depending on the load applied by the dilatometer.

(Table 2). Conventionally, technologists do not report viscosities in terms of values found at given temperatures, but rather in terms of temperatures at which given viscosity values are obtained. Thus, $T(n.n)$, the *isokom* temperature, denotes the temperature in °C at which the melt assumes a value $\log \eta = n.n$ in poise CGS units (1 P = 0.1 Pa·s so that all values compiled in Table 1 have to be decreased by 1 if one retains instead the Pa·s SI unit used in many recent publications). The importance of reporting temperatures instead of viscosities rests on the facts that the (Newtonian) rheological response of all substances is by definition the same at the same viscosity and that only the temperature of a glass – not its viscosity – can be operationally regulated during the various forming, tempering, annealing, or cooling steps of glass making.

Viscosity–temperature relationships do vary much with chemical composition: as illustrated in Figure 3 by the data for a soda-lime float glass, a stonewool and silica

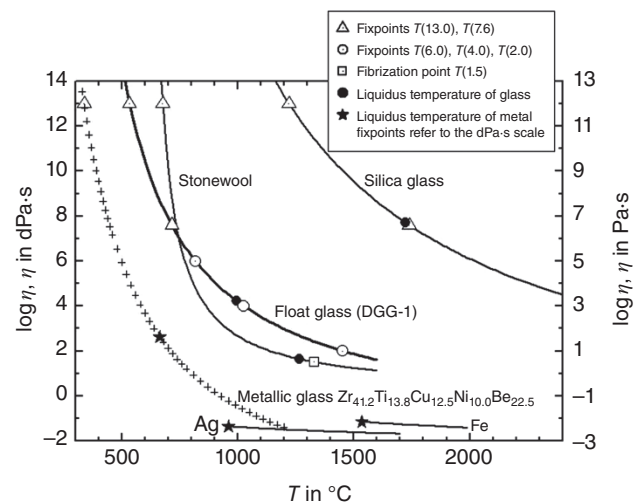


Figure 3 Viscosity–temperature relationship of different glass-forming systems; pure metallic melts of Ag and Fe are displayed for comparison.

glass, and those for a bulk metallic glass and pure Ag and Fe liquids. The fixed points of Table 1 are pinpointed for each glass melt and read in this graph, as just explained, starting from its Y axis. The complete viscosity curves can be reproduced by Vogel–Fulcher–Tamman (VFT) equations,

$$\log \eta = A + B/(T - T_0), \quad (2)$$

where A , B , and T_0 are empirical fit constants and T is expressed here in $^{\circ}\text{C}$. The float glass DGG-1 included in Figure 3 is a certified viscosity standard whose VFT equation has been derived from 44 measurement points. These are reproduced with the parameters $A = -1.601$, $B = 4330.9$, and $T_0 = 246.1$ (η in dPa·s) with a standard deviation of $\delta \log \eta = \pm 0.16$, illustrating that the VFT equation is a valuable tool for any technological purpose.

Viscosities are in addition an indicator of crystallization tendency at the liquidus temperature T_{liq} , which is shown in Figure 3 on the viscosity curves. Melts with $\log \eta(T_{\text{liq}}) < 2.0$ tend to crystallize quickly, thus requiring very high cooling rates, whereas melts with $\eta(T_{\text{liq}}) > 4.0$ may in contrast be vitrified at moderately low cooling rates.

Of great interest, therefore, is the possibility to predict the viscosity of a glass melt as a function of its temperature

and chemical composition. From measurements performed for a variety of samples, sets of incremental factors have been empirically derived by regression analysis for this purpose. The left-hand part of Table 3 presents such a widely used database [19] with which the effect of additions of individual oxides (by weight and molar amounts, respectively) have been calculated for a soda-lime silicate. The temperature $T(\text{n.n})$ at which viscosity reaches $10^{\text{n.n}}$ dPa·s is thus calculated as

$$T(\text{n.n}) = a(\text{SiO}_2) + 100 \cdot \sum a(j) \cdot y(j)/y(\text{SiO}_2), \quad (3)$$

where $y(j)$ is the weight fraction of oxide j .

Helpful guidelines for the design of the viscosity curve of a mass-produced glass may be derived from the graphs of Figure 4. For example, replacement of 1 wt % SiO_2 by 1 wt % Li_2O to yield a glass 73 wt % SiO_2 , 10 CaO, 16 Na_2O , 1 Li_2O lowers the temperature at $\log \eta = 4.0$ and 13.0, relative to the base glass, by 45 and 29 K, respectively. Among the *alkali oxides*, lithia is the strongest liquidus flux; it significantly lowers viscosity at all levels. *Boron oxide* has a similarly strong effect, however, at high-temperature only. So it reduces the working range (the

Table 3 Empirical factors for the calculation of viscosities [19] and elastic properties [21, 22] (units revisited) from composition.

Oxide j	Viscosity				Elastic properties	
	$a(j)$ for			Validity range (wt %)	$V(j)$ (cm^3/mol)	$U(j)$ (GPa)
	$T(2.0)$ ($^{\circ}\text{C}$)	$T(4.0)$ ($^{\circ}\text{C}$)	$T(6.0)$ ($^{\circ}\text{C}$)			
SiO_2	1847.80	1249.70	962.90	60–77 ^a	28.0	64.5
TiO_2	−4.00	−4.00	−4.00	0–8 ^b	29.2	86.7
ZrO_2	8.65	7.96	8.16	0–8 ^b	30.2	97.1
Al_2O_3	8.32	5.23	4.01	0–8 ^a	42.8	134.0
B_2O_3	−21.62	−11.97	−6.42	0–14 ^a	41.6	77.8
– “–	0.5122	0.3182	0.1900	— ^c	—	—
MgO	−5.87	−0.12	0.91	0–6 ^a	15.2	83.7
CaO	−11.27	−3.99	−0.74	4–13 ^a	18.8	64.9
BaO	−5.67	−3.04	−1.88	0–17 ^b	26.2	40.6
ZnO	−5.37	−1.99	−0.71	0–9 ^b	15.8	41.5
PbO	−4.85	−3.17	−2.24	0–12 ^b	23.4	17.6
Li_2O	−35.54	−30.04	−26.45	0–3 ^a	16.0	80.4
Na_2O	−12.65	−9.19	−7.06	10–17 ^a	22.4	37.3
K_2O	−5.93	−4.17	−3.53	0–9 ^a	37.6	23.4
Error	± 4.7 K	± 3.4 K	± 3.2 K	—	n.s.	n.s.

^a Combinations of these oxides, plus one.

^b Oxide only, keep the error within the given $\pm$ range.

^c For boron oxide, the factors in the second row are square terms; thus, the sum for each $T(\text{n.n})$ has to be expanded by a term $10\,000 \cdot a(\text{B}_2\text{O}_3) \cdot [y(\text{B}_2\text{O}_3)/y(\text{SiO}_2)]^2$.

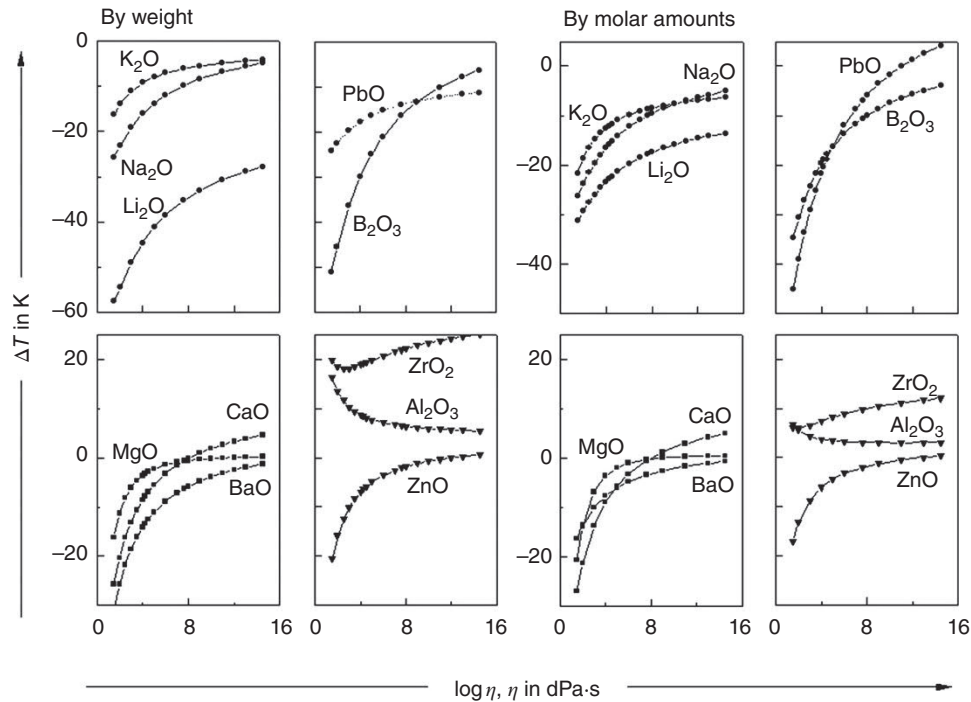


Figure 4 Temperature change brought about by a replacement of 1% of SiO_2 by another oxide in the base glass composition 74 SiO_2 , 10 CaO , 16 Na_2O ; left side: for oxide amounts by wt; right side: for molar amounts.

“length”) of a glass. In the language of glass technologists, boron oxide makes a glass “short.” Lime strongly reduces viscosity at high temperatures; the effect is almost as strong as with soda. Thus, if viscosity needs to be lowered in this range, inexpensive limestone as a calcium carrier raw material may be used instead of expensive soda ash as a sodium carrier. Also note that lime, quite in contrast to *magnesia*, makes a glass “short.” One can thus extend the working range of a glass by manipulating its CaO/MgO ratio. *Alumina* makes at the same time a glass more viscous and “longer.” Although not giving any in-depth scientific understanding, these empirical tools undoubtedly have their merits in glass technology.

3.2 Liquidus Temperatures

Most industrial glass-melting processes run in a continuous way 365 days per year over periods of 2–15 years. This operation time depends on the type of glass and on the corrosion wear of both the refractory lining of the melting tank and channels guiding the melt to the working stations. A maximum temperature of about 1500 °C is needed to achieve homogenous fusion; at the exit of the furnace, the melt still is at about 1350 °C. This temperature makes it necessary to cool steadily the melt down to $T(3.0)$ while keeping a safety margin ΔT above the liquidus temperature T_{liq} of the particular composition to prevent precipitation of crystals. This

yields a constraint of a minimum temperature of $T(3.0) + \Delta T$ required to ensure a crystal-free glass. This constraint is especially critical for continuous glass fiber production (Chapter 1.5), but it applies to any other process as well before the forming step.

Traditionally, liquidus temperatures have been determined experimentally to be represented graphically for simple-enough systems in the form of phase diagrams (Chapter 5.2, [2]). For complex compositions of industrial interest, they are generally determined with a gradient furnace whereby a series of 5–10 samples are heated for typically 24 hours in a temperature gradient spanning the expected range of T_{liq} . After quenching, the samples are examined by optical microscopy. The liquidus temperature is then bracketed by the treatment temperatures of the last homogeneous glass and that of the first sample in which crystallites are observed. In a more accurate approach, samples from the gradient furnace containing tiny amounts of crystals are reheated in a heating-stage microscope at a rate well below 1 K/min, and the temperature at which the last crystal dissolves is adopted as T_{liq} .

Thanks to the progress made in thermodynamic modeling of melts (Chapter 5.3), an increasingly useful approach is to predict liquidus temperatures with one of the dedicated softwares designed to calculate phase equilibria relevant to glass making (e.g. 20). Empirically, however, simple rules have long been known to predict

the effects on a given oxide on liquidus temperatures. Illustrating again the predominantly pairwise nature of atomic interactions, they rely particularly on the topology of binary phase diagrams (Figure 5). The tremendous freezing-point depressions of SiO_2 brought about by addition of alkali oxides as well as by boron and lead oxides are in fact so conspicuous that they have historically been at the basis of the development of glass technology. As illustrated by a comparison made between Li_2O and K_2O (Figures 4 and 5), of particular interest is the fact that

the alkali oxide that most strongly decreases viscosity is the least effective in lowering liquidus. Only boron and lead oxides cause strong decreases of both viscosity and liquidus. This may shed some light on the technological challenge raised by the replacement of lead oxide in the glass formulae of modern tableware and solder glasses.

In ternary systems, the Na_2O – CaO – SiO_2 and CaO – Al_2O_3 – SiO_2 phase diagrams are especially important as they serve as references for soda-lime and most stoneware and reinforcement-fiber glasses, respectively (Figure 6).

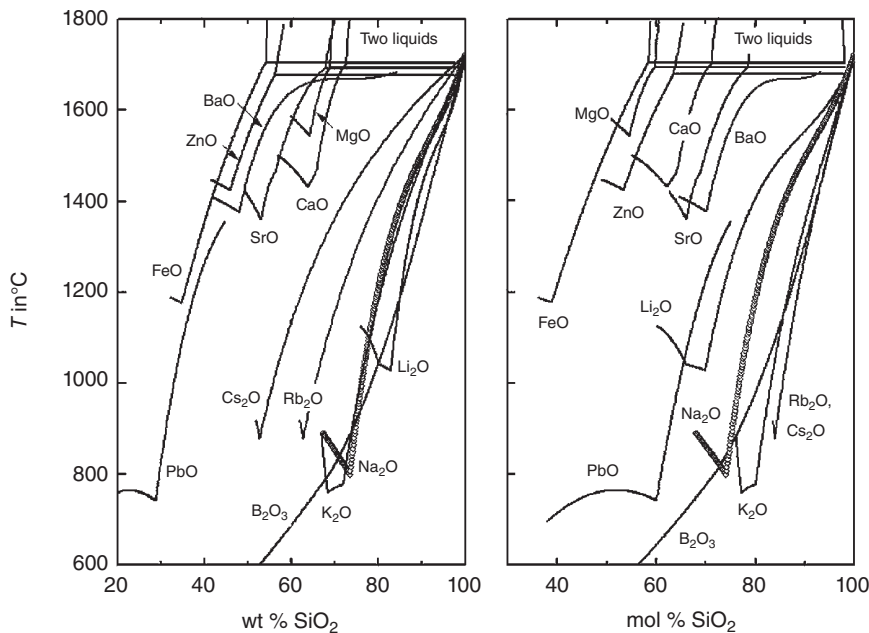


Figure 5 Liquidus lines of binary silicate systems (left: by wt, right: by mol); all systems comprising a divalent oxide, except BaO, show an extended stable miscibility gap; data source [2].

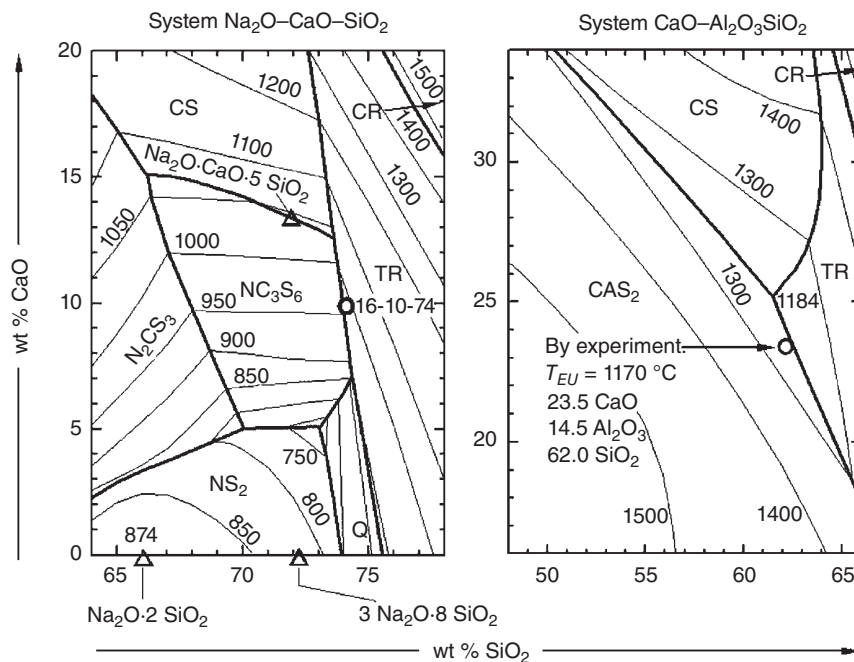
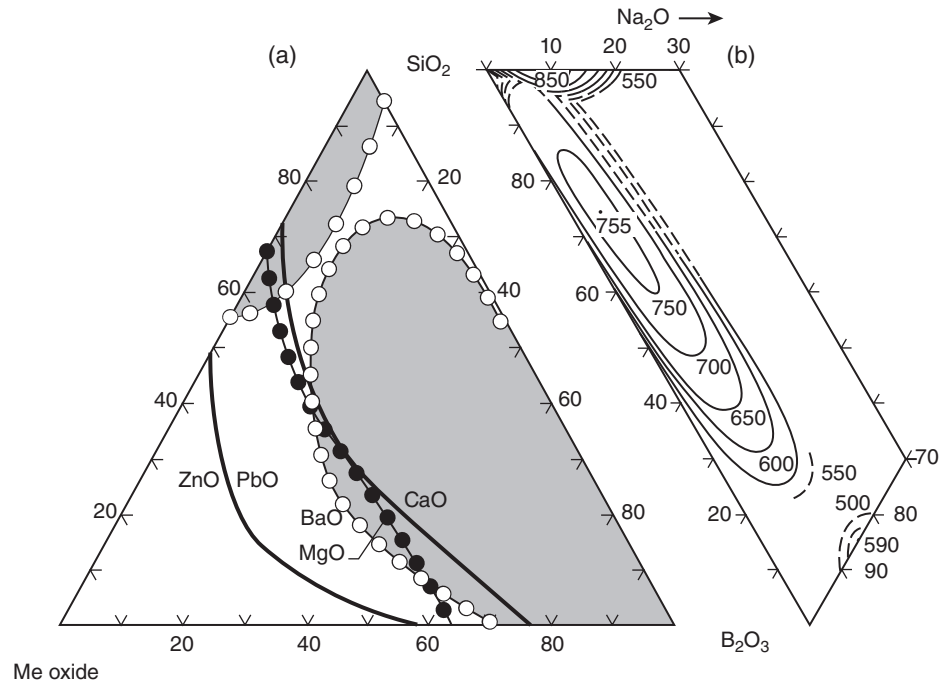


Figure 6 Ternary phase diagrams in versions of technological relevance; shorthand notation: N = Na_2O , C = CaO , A = Al_2O_3 , S = SiO_2 , Q = quartz, TR = tridymite, CR = cristobalite; left: the basic system of all commercial hollowware and flat glasses; the triangles mark the positions of the compounds, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$; the circle the position of the base glass 74 SiO_2 , 10 CaO , 16 Na_2O ; data source [2]. Right: the basic system of reinforcement-fiber glasses; industrial compositions flock around the eutectic; calculation using FactSage® [23].

Figure 7 Miscibility gaps. (a) Extension of stable gaps in ternary borosilicate systems with different oxides as third component; the area shaded in gray refers to BaO; (b) isotherms of the (metastable) subliquidus immiscibility dome in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$.



From Figure 6a, it is easy to understand why, in Antiquity (Chapter 10.3), glasses with silica contents of 70–74 wt % and amounts of lime not exceeding 12 wt % were already mass produced: Thanks to typical $T(3.0)$ values of $1200 \pm 10^\circ\text{C}$, it is comparatively easy to comply for them with the constraint $T_{\min} = T(3.0) + \Delta T$. The particular composition “16-10-74” has been investigated in many scientific studies. It may be considered as a reference and the *mother* of all mass-produced glasses, including of course today’s float glass. That the $T_{\min}$ constraint represents in contrast a real challenge for $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ -based glasses is readily apparent in Figure 6b where only a narrow range around the ternary eutectic between tridymite [SiO_2], wollastonite [CaSiO_3], and anorthite [$\text{CaAl}_2\text{Si}_2\text{O}_8$] qualifies for a successful production. In passing, note that Figure 6b has been calculated by using the thermochemical software and databases FactSage® [23]. The experimental position of the mentioned eutectic is also marked, thus displaying the degree of accuracy that may be expected from the calculation of liquidus for more complex compositions.

3.3 Liquid–liquid unmixing

If phase separation within a condensed system most commonly takes place via partial crystallization, it can also occur as liquid–liquid unmixing (Chapter 5.2). Ternary systems containing boron oxide illustrate that the phenomenon should certainly not be overlooked in glass-forming systems. For ternary borosilicates, the boundaries of the composition domains where such an unmixing

takes place stably, i.e. above the liquidus, are indicated in Figure 7a. If temperature is represented in a third dimension, these domains define the base areas of immiscibility domes that eventually terminate at upper critical points at their tops. The isotherms of the immiscibility dome in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$, which is the base composition of all borosilicate glasses, are drawn in Figure 7b. Here, in contrast to Figure 7a, the entire dome comprising its upper critical point (755°C at composition 25-05-70 by wt) is located below the liquidus surface. Hence, liquid unmixing cannot take place during the initial melting step, but at lower temperatures during the forming process. This is one of the reasons why, in order to minimize phase-separation effects, pharmaceutical and low-expansion borosilicate glasses are designed around a composition of 80 wt % silica. The system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ (not shown here) displays a similar topology.

It is only with glasses known under the trade name *Vycor Glass* that liquid unmixing is exploited on purpose. Here, after forming by conventional technology to the desired shape, phase separation develops upon annealing at an appropriate temperature to yield two interconnected phases, namely an Na_2O - and B_2O_3 -rich glass along with another one that contains more than 96 wt % SiO_2 . Then the former is leached out by a hot strong mineral acid, leaving behind a nanoporous skeleton of high- SiO_2 glass. This material may then be used directly as filter, for example, or sintered at temperatures below 1300°C to fabricate dense and almost pure silica glass articles much more readily than with pure SiO_2 .

The numerical calculation of liquid–liquid immiscibility ranges in multicomponent systems (e.g. by using the software and databases mentioned in Section 3.2) is even more challenging than the calculation of solid–liquid equilibria. This is because available experimental data hardly reach beyond what has been sketched in the present section, and such a narrow base of information does not allow to fine-tune the parameters used in the calculations.

4 Glass Composition – its Relevance to Glass Properties

4.1 Property Optimization

Both search and optimization of glass formulae begin with a given profile of target glass properties. In the following, three properties will be addressed as examples typically targeted in glass development, namely the elastic properties, the thermal expansion coefficient, and the chemical durability. From a scientific point of view, such a task should rest on deep insights on the relationships between chemical composition, glass structure, and glass properties. It is only from such a fundamental approach that ground-breaking developments of novel glasses with outstanding properties may be expected. But this goal is still a matter of fundamental research as expounded in the following chapters where this most challenging issue is pursued.

For the time being, however, only few manageable tools and procedures of this kind are available for the technological community. To optimize properties, technologists thus rely largely on empirical approaches whereby, as applied to glass viscosity in Section 3.1, they use incremental oxide factors derived by statistical means from large numbers of experiments. One has, however, to keep in mind that these approaches represent only interpolations of what is already known. Hence, limited areas in compositional space leading to truly outstanding properties should be easily overlooked so that developments similar to the famous low-expansion metallic alloy *Invar* are very unlikely to be found this way.

4.2 Elastic Properties

Incremental oxide factors for the calculation of the elastic properties from the composition compiled in the right-hand part of Table 3 are taken from a widely accepted earlier publication [21]; for the sake of clarity, they have been adjusted with respect to the units used, i.e. to cm^3/mol for volume, and to GPa for modulus increments. Young's modulus E is then calculated with

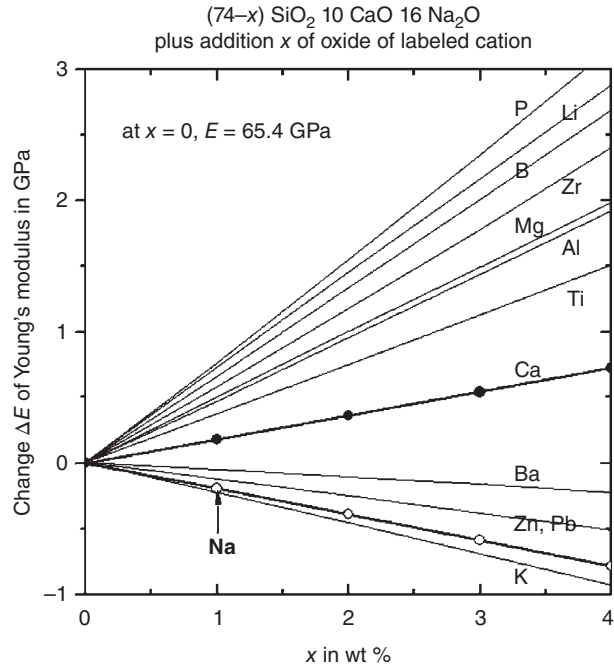


Figure 8 Change of Young's modulus E in the base glass composition 74 SiO_2 10 CaO $16 \text{ Na}_2\text{O}$ upon the replacement of x wt % silica by another oxide.

$$E = [\rho \cdot \sum V(j) \cdot x(j) / \sum M(j) \cdot x(j)] \cdot \sum U(j) \cdot x(j), \quad (4)$$

where $x(j)$ and $M(j)$ are the mole fraction and molar mass of oxide j , respectively, and ρ the density of the glass.

As for Poisson's ratio μ , it is calculated as

$$\mu = 0.5 - 0.278 / [\rho \cdot \sum V(j) \cdot x(j) / \sum M(j) \cdot x(j)]. \quad (5)$$

The manner in which Young's modulus varies when a glass composition of $(74 - x)\text{SiO}_2$, 10 CO , $16 \text{ Na}_2\text{O}$ (by wt) is modified by an addition of x wt % of another oxide is illustrated in Figure 8. Young's modulus can be raised by the addition of P, Li, B, Zr, Mg, and Al oxides, and in contrast lowered by oxides of heavy mono- and divalent ion oxides. True, such small additions do not yield major overall effects but the tendency is clearly shown.

4.3 Thermal Expansion Coefficient

Incremental oxide factors for the calculation of the thermal expansion coefficient are compiled in Table 4. Again, the factors are taken from a widely accepted earlier publication [24], see also [15]. When inspecting the entries in Table 4, the reader will notice a number of conditions that have to be obeyed for specific compositions. These conditions reflect intrinsic structural changes, which

Table 4 Empirical factors for the calculation of the thermal expansion coefficient α_{20-300} in ppm/K; it is calculated from the molar fractions of oxides j like $\alpha_{20-300} = \sum x(j) \cdot \alpha(j)$.

Oxide j	Increment $\alpha(j)$	Condition
SiO ₂	10.5–10· $x(\text{SiO}_2)$	$x(\text{SiO}_2) > 0.67$
	3.8	Otherwise
TiO ₂	10.5–15· $x(\text{SiO}_2)$	$0.5 < x(\text{SiO}_2) < 0.8$
ZrO ₂	–6.0	
Al ₂ O ₃	–3.0	
B ₂ O ₃	–1.26· φ	$\varphi < 4$
	–5.0	Otherwise
MgO	6.0	
CaO	13.0	
BaO	20.0	
MnO	10.5	
ZnO	5.0	
PbO	13.0	$\sum x(\text{R}_2\text{O}) < 0.03$
	13.0	$(1/\psi) \cdot \sum x(\text{R}_2\text{O}) < 3$
	$11.5 + 0.5 \cdot \sum x(\text{R}_2\text{O})$	Otherwise
Li ₂ O	27.0	
Na ₂ O	41.0	in Na ₂ O–SiO ₂
	39.5	Otherwise
K ₂ O	46.5	in K ₂ O–SiO ₂
	42.0	Otherwise

$\varphi = (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{BaO} + 0.7 \cdot \text{CaO} + 0.7 \cdot \text{PbO} + 0.3 \cdot \text{Li}_2\text{O} + 0.3 \cdot \text{MgO} + 0.3 \cdot \text{ZnO} - \text{Al}_2\text{O}_3) / \text{B}_2\text{O}_3$;

$\psi = \sum (\text{RO} + \text{R}_2\text{O}_3 + \text{R}_2\text{O}_5)$;

Oxide amounts to be inserted as molar fractions.

can be understood only if the chapters in Part II are consulted. As an example, the sophisticated condition for the increment of boron oxide by the factor φ reflects the expected coordination change between $[\text{BO}_3]$ and $[\text{BO}_4]$ units in the glass (Chapter 7.6). Predictions based on these factors yield estimates of the thermal expansion coefficient within an error margin of ± 0.3 ppm/K. The effect of addition of x wt % of another oxide is shown in Figure 9 for the base glass composition 74 SiO₂·10 CaO·(16– x) Na₂O. Clearly, alkali oxides raise the thermal expansion coefficient whereas especially oxides of highly charged ions decrease it. Iso lines of the expansion coefficient within the ternary sodium borosilicate system are plotted in Figure 10. Optional compositions for so-called “hard” glasses with $\alpha = 4$ ppm/K are marked. The base composition 6 Na₂O·10 B₂O₃·84 SiO₂ may be considered as a starting point for further adjustment. When taking $6 \text{ Na}_2\text{O} \rightarrow 4 \text{ Na}_2\text{O}$, $10 \text{ B}_2\text{O}_3 \rightarrow 13 \text{ B}_2\text{O}_3$, $84 \text{ SiO}_2 \rightarrow 81 \text{ SiO}_2 + 2 \text{ Al}_2\text{O}_3$, then the composition obtained is

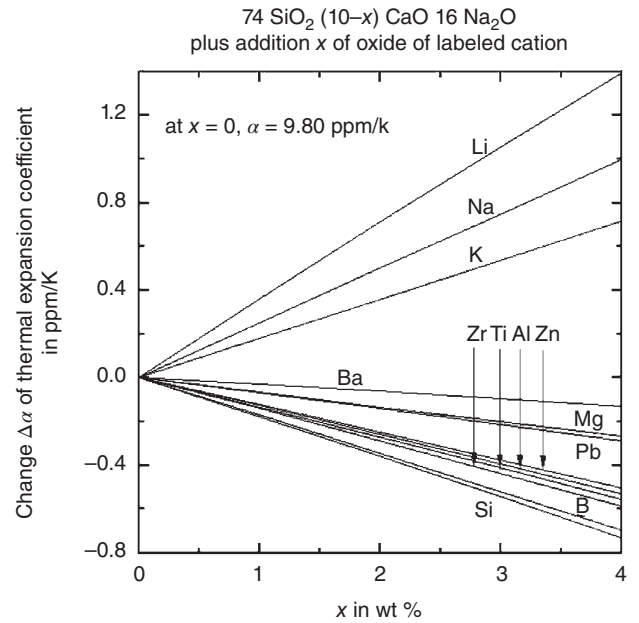


Figure 9 Change of the thermal expansion coefficient α_{20-300} in the base glass composition 74 SiO₂ 10 CaO 16 Na₂O upon the replacement of x wt % of calcia by another oxide.

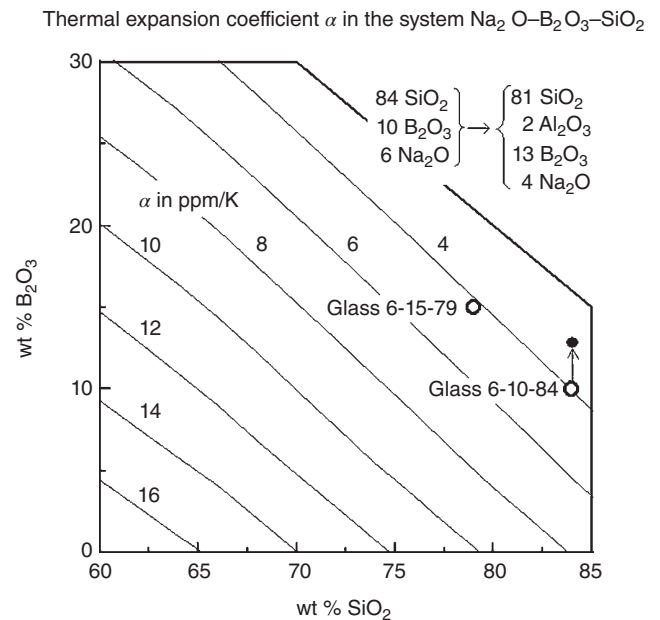


Figure 10 Ternary composition diagram of the system Na₂O–B₂O₃–SiO₂ showing iso lines of the thermal expansion coefficient α_{20-300} ; base glass compositions reaching coefficient $\alpha_{20-300} = 4.0$ ppm/K are highlighted; the further development strategy toward an industrial product is sketched in the upper right corner and indicated by the arrow.

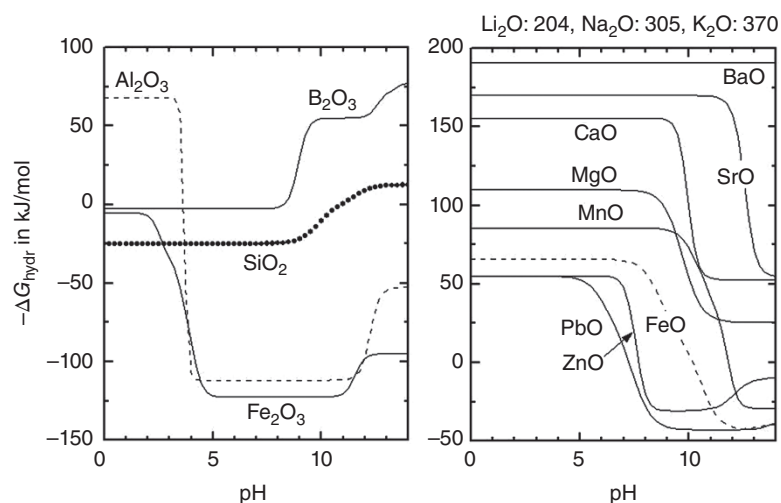


Figure 11 Hydrolytic stability of different pure oxides in aqueous solution as a function of pH; the stability is given in terms of Gibbs energy of hydration ΔG_{hydr} ; negative values of ΔG_{hydr} are plotted against pH to make the most stable cases appear at the bottom of the graphs.

indeed very similar to those of the commercial products *Duran* or *Pyrex* having a thermal coefficient of expansion $\alpha_{20-300} = 3.3 \text{ ppm/K}$ between 20 and 300 °C.

4.4 Chemical Durability

Chemical durability is a very complex property. Attempts at generating an oxide increment system for the prediction of this property are not recommended because the most basic information on chemical durability must reflect the stability of a glass in strong acids, neutral water, and strong caustic solutions. Irrespective of their role in the glass structure, even pure oxides exhibit quite a complicated stability pattern as a function of the solution pH. This is shown in Figure 11 (from [25], revised version). Clearly, a general statement like “alumina enhances the chemical durability of a glass” is erroneous. It is true, alumina enhances the chemical durability under moderately acid to fairly caustic conditions, but it destabilizes a glass exposed to strong acids. Anyway, Figure 11 provides a first guideline of the effect which may be expected from a specific oxide in a given pH range, and hence, to base a first step of development on this information. In Chapter 5.11, the approach is further elaborated.

5 Perspectives

Challenges for future development mainly deal with the extension of both thermochemical and thermophysical databases for glass-forming systems. The usefulness of phase diagrams and of thermochemical calculations for glass development has been demonstrated. Yet, when it comes to the databases on which the calculations of phase diagrams rest, a severe lack of results for multicomponent melts relevant to the glass industry is felt. This situation is

due to the fact that the extension of databases is chiefly driven by the financially potent metallurgical industry whose compositional focus distinctly differs from the needs of the glass industry. A reliable approach to liquidus temperatures, even for the conventional container, float, or fiber glass branches, would open doors for significant process improvements, resulting in enhanced sand dissolution upon melting, higher pull rates, energy saving, enhanced glass quality, and reduced loss of expensive glass contact materials like platinum.

Whereas thermochemical data sets (standard enthalpies and entropies, C_p polynomials) are available for about 6000 mineral substances, thermophysical standard data sets (including stiffness parameters, and their temperature coefficients) hardly exceed a number of a few hundreds only [26]. From such data, glass technologists might learn how the local atomic structure of a material in general influences the resulting mechanical properties. Thus, to date, the intense quest for stronger glasses rests on an extremely narrow scientific basis. The same is true for the adjustment of the thermal expansion coefficient of solder glasses and substrate glasses to contact materials with very high or very low thermal expansion coefficient (like copper, alumina, steel, or silica glass, low-expansion glass ceramics, respectively).

As stated above, as useful as the conventional oxide increment systems may be in the daily routine of industrial glass development, an approach to truly novel glass compositions with outstanding properties must be based on a deep understanding of the relation between chemical composition, structure, and properties. This is where the field of atomistic simulation should play a decisive role in a near future (cf. Chapters 2.7 and 2.8). The challenge for the coming decades thus consists in developing first-principles tools suitable for industrial applications.

Beyond this, new glass-forming systems with a high potential for application as functional materials are being developed. As described in Chapter 8.9, an important group with relevance at the industrial scale (not shown in the scheme of Figure 1) are hybrid glasses combining both inorganic and organic bonds in their structure. Such glasses have been synthesized via a sol–gel route for a long time (Chapter 8.2); recently, systems accessible by melting have been presented [27].

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1.2

Raw Materials for Glassmaking: Properties and Constraints

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1 Introduction

Even though industrial glasses may now be transported across the planet, glassmaking tends to remain a local industry. When selecting their raw materials, glassmakers target specific oxides or elements to fit quantitatively a calculated recipe [1, 2] by paying special attention not only to their composition and quality but, of course, also to their price. Raw materials in effect may represent up to one third of the total cost of glassmaking, strongly depending on local geographical and logistic conditions such as quarry-to-plant distance or transportation mode, which can be by waterways, rail, or truck. This concern holds especially true for commodity products which, like hollow ware, are facing fierce competition from metal or plastic materials.

Natural materials are in principle favored because, like for the mineral resources used in metallurgy or cement industry, their extraction, milling, and transportation are relatively inexpensive operations compared to the fabrication cost of synthetic materials. Some of the raw materials used in glassmaking must nonetheless be man-made when their natural counterparts are rare, geographically restrained, or of an insufficient purity. As such, their price can dramatically increase the overall batch cost. For instance, synthetic sodium carbonate may constitute up to 50 % of the total batch cost for window or bottle glass, whereas it constitutes less than 14 wt % of the recipe.

After batch preparation, melting and subsequent chemical homogenization are complex processes whose kinetics depend on a number of factors. The grain size distribution of raw materials is particularly important in this respect as the main starting product, quartz, dissolves into the forming melt at a rate of only a few hundred μm per hour, so that pull rates tremendously decrease with increasing grain size. The impurity content is another fundamental issue. As natural products, most raw materials are far from being pure chemicals. The infusible minerals they may bring in have a very high likelihood of surviving the glassmaking process and, therefore, of causing unacceptable production losses even when present at the ppb levels. Other impurities such as iron metal originate in the initial processing of the raw materials. In any case, impurities may cause raw materials to depart from the specified physical and chemical properties. Production yield and quality can then be strongly impacted.

Since many parameters may have either positive or negative consequences if not properly mastered, an in-depth knowledge of the chemical and physical properties of raw materials is necessary. In this chapter, the main chemical, physical, engineering, and economic criteria pertaining to raw materials specifications will thus be reviewed. Because high production yields cannot be obtained without high-quality and permanently controlled raw materials, attention will be paid to production problems most commonly met if the specifications and management of raw materials are not respected. The focus will be here on the raw materials used for silicate glasses manufactured in very large quantities. For specialty glasses, the reader is referred to the chapters that deal specifically with optical fibers (Chapter 6.4), chalcogenide (Chapter 6.5) or metallic glasses (Chapter 7.10), sol-gel products (Chapter 8.2), or bioglass (Chapter 8.4).

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2 Raw-material Specifications

2.1 The Specificity of Raw Materials

A very great many different raw materials can be used today for batch preparation (Table 1). On a chemical and mineralogical basis, they can be classified as silicates, carbonates, borates, oxides, and hydroxides. Recycled glass, known as *cullet* (cf. Chapter 9.9), as well as industrial by-products such as metallurgical slags can in addition enter the batch preparation as amorphous and chemically complex materials. As apparent in Figure 1, the compositions of these materials do not match those of the main glass products, which may thus need up to a dozen ingredients for batch preparation. Even the most common soda-lime silica glasses, circled in Figure 1, manufactured for building (windows), automotive (windshields), packaging (bottles), and solar (photo-voltaic panels) applications, require several of them.

Each raw material plays a specific role. Most of them, as oxides, form the building blocks of the glass network as formers or modifiers (see Chapters 20.4 and 2.5), but among the latter some act as fluxes (alkalis), strengthening agents (alkaline earths), refiners (Na sulfate, Sb, Sn, As oxides), reducers (coke, slags), or even as oxidizing, O_2 -releasing ($BaNO_3$), or coloring (Fe, Cr, Mn, Co, etc.) agents.

Raw materials react in specific ways within the batch. Some are strongly hygroscopic, influencing as such the rheology and homogeneity of the still solid batch. As a matter of fact, water is present in most of the raw materials used to produce glass as either free water (moisture) or bound in the crystal structure of minerals. This essential and unavoidable component is crucial in raw-material management since it minimizes the formation of dust at both the batch plant and the dog-house (entrance of the furnace) levels, but it may also contribute to the formation of lumps made of the most hygroscopic materials, increasing the heterogeneity of the batch at the very beginning of melting. Furthermore, as a result, the batch may contain up to few wt % of water, whereas there are less than 1000 ppm H_2O in the final glass. Removing the water in excess may cost much in terms of both energy and furnace refractories, which may be corroded by acids such as HF and HCl formed when water reacts with other volatile components of the batch.

Without taking into account the formation of intermediate products, the overall meltability of the raw materials is highly variable [3]: H_2O is released at around 100 °C; the deshydroxilation of OH-bearing minerals takes place at 400–800 °C; carbonates release large quantities of CO_2 at 700–900 °C; feldspars melt below 1200 °C; the other

silicates are dissolved in the pre-existing glass melt above that range; bauxite has an even stronger refractory character, needing temperature above 1300 °C to be digested by the surrounding liquid (cf. the DSC thermogram of Figure 3, in Chapter. 1.5).

Suppliers of raw materials process their products through several steps to match their customers' specifications [4]. First, rocks containing the desired raw material(s) are blasted or excavated. The bulk material so extracted is then retrieved, crushed, ground, screened, and sorted to achieve the required grain size, washed, dried, or dewatered before being stockpiled and transported in big bags or in bulk. In some cases a physical and/or chemical beneficiation stage may be needed to achieve the required specifications, especially to remove unwanted impurities. All these steps can have an impact on the final quality of the raw materials in terms of presence of impurities and heterogeneities.

2.2 Grain Size

The particle (or grain) size distribution (PSD) is a crucial parameter of individual raw materials. The required PSD may be costly to achieve. It primarily depends on the hardness of the bulk material, which in turn roughly correlates with its melting temperature [5]. As examples, K-feldspar has a hardness of 6 (out of a maximum of 10) on the Mohs scale and melts at about 1200 °C, quartz has a hardness of 7 and melts above 1700 °C (in the form of cristobalite), whereas corundum ($\alpha-Al_2O_3$) has a hardness of 9 and melts above 2000 °C. Hence, the glassmaker determines the final PSD of the raw material as a compromise between meltability, furnace technology, and price (cost) while also limiting the unnecessary fines that generate dust and furnace carryovers. For specific applications, the glassmaker may in addition request the supplier of raw material to cut the lower end of the PSD to get totally rid of dust from fines.

The sieve PSD curves of a variety of important raw materials are compared in Figure 2 to illustrate their variations with composition and overall batch meltability. The median diameter representing 50% of a sieved raw material is termed D50. For quartz, it ranges from 200 to 300 μm when sand is used for standard window or bottle glass but is much lower at 50–100 μm for the flour, for instance, used as SiO_2 -carrier for E-glass fiber, a peraluminous, boron-bearing, alkaline earth silicate (Chapter 1.5). At the other end, the D50 of limestone and dolomite may exceed 1 mm and that of basalt for insulating glass applications may even be 10 times larger because chemical heterogeneities are in this case much smaller than within a mixture of raw materials.

Table 1 Natural and *synthetic* raw materials compositions and prices.

Oxide	Raw material	Bulk chemistry	Overall mineralogy	Sp – Fr – It – De	Price €/T*
SiO ₂	Quartz-sand	>95 % SiO ₂ ; H ₂ O, Al ₂ O ₃ , RO, R ₂ O, Fe ₂ O ₃	Quartz, free-water, mica, feldspars	Arena – Sable – Sabbia – Sand	20–200€/T
	Sandstone	>95 % SiO ₂ ; H ₂ O, Al ₂ O ₃ , RO, R ₂ O, Fe ₂ O ₃	Quartz, mica, feldspars, FeTi-oxides, free-water	Arenisca – Grès – Arenaria – Sandstein	
	Quartzite	>95 % SiO ₂ ; H ₂ O, Al ₂ O ₃ , RO, R ₂ O, Fe ₂ O ₃	Quartz, mica, feldspars, FeTi-oxides	Cuarcita – Quartzite – Quarzite – Quarzit	
Al ₂ O ₃ , R ₂ O	Feldspar (concentrates from greywacke, arkose, pegmatite, granite, etc.)	17–20 % Al ₂ O ₃ ; 11–15 % R ₂ O; <65 % SiO ₂ ; H ₂ O; Fe ₂ O ₃ , TiO ₂ , CaO	Alkali-feldspars [(K,Na)AlSi ₃ O ₈ : orthoclase, microcline, sanidine, albite, and their solid solutions], quartz (15–20%), micas. Li-rich (up to 1.5 wt %) contain spodumene, petalite, or lepidolite (Li-mica), mainly.	Feldespato – Feldspath – Feldspato – Feldspat	80–150€/T
	Nepheline(–syenite)	20–26 % Al ₂ O ₃ ; 15–18 % R ₂ O; <56 % SiO ₂ ; H ₂ O; Fe ₂ O ₃ , TiO ₂ , CaO	Alkali-feldspars [(K,Na)AlSi ₃ O ₈ : microcline, sanidine, albite, and their solid solutions], alkali-feldspatoids [(K,Na)AlSiO ₄ : nepheline, kalsilite, and their solid solutions], micas, titanite, perovskite, garnet, zircon, apatite, REE-silicates. Silica undersaturated = no quartz	Nefelina – Néphéline – Nefelina – Nephelin	100–130€/T
	Phonolite	20–26 % Al ₂ O ₃ ; 15–18 % R ₂ O; <56 % SiO ₂ ; H ₂ O; Fe ₂ O ₃ , TiO ₂ , CaO	Alkali-feldspars [(K,Na)AlSi ₃ O ₈ : sanidine, albite, and their solid,solutions], alkali-feldspatoids [(K,Na)AlSiO ₄ : nepheline, kalsilite, and their solid,solutions], leucite KAlSi ₂ O ₆ , sodalite, haiüyne, carnegeite, micas, amphibole, pyroxene, titanite, ilmenite, perovskite. Silica undersaturated = no quartz	Fonolita – Phonolite – Fonolite – Phonolith	60–70€/T
	Anorthosite	<30 % Al ₂ O ₃ , <15 % CaO, <45 % SiO ₂ , Fe ₂ O ₃ , R ₂ O, MgO	Anorthite CaAl ₂ Si ₂ O ₈ , pyroxene, amphibole		
Al ₂ O ₃	Bauxite (raw or calcined)	40 % < Al ₂ O ₃ < 80 %; 10–15 % Fe ₂ O ₃ ; H ₂ O; SiO ₂	Gibbsite Al(OH) ₃ , diaspore α-AlO(OH), boehmite γ-AlO(OH), bayerite, corundum, goethite, hematite, kaolin, anatase	Bauxita – Bauxite – Bauxite – Bauxit	250–400€/T
	Hydrated alumina	>60 % Al ₂ O ₃ , H ₂ O, Fe ₂ O ₃ , SiO ₂	Al(OH) ₃ polymorphs		250–300€/T
	Calcined alumina	99 % Al ₂ O ₃ , Fe ₂ O ₃ , SiO ₂	Corundum		500–600€/T
	Kaoline	>45 % SiO ₂ , >35 % Al ₂ O ₃ , 13–14 % H ₂ O, Fe ₂ O ₃	Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄ , quartz	Caolín – Kaolin – Caolino – Kaolin	100–300 €/T
	Pyrophyllite	>65 % SiO ₂ , >25 % Al ₂ O ₃ , H ₂ O	Pyrophyllite Al ₂ Si ₄ O ₁₀ (OH) ₂ , quartz		

(Continued)

Table 1 (Continued)

Oxide	Raw material	Bulk chemistry	Overall mineralogy	Sp – Fr – It – De	Price €/T*
Na ₂ O	<i>Na-carbonate (soda ash)</i>	58 % Na ₂ O, 42 % CO ₂	<i>Natrite</i> Na ₂ CO ₃ , <i>natron</i> Na ₂ (CO ₃) · 10 H ₂ O, <i>trona</i> Na ₂ CO ₃ · NaHCO ₃ · 2 H ₂ O	<i>Soda – Na-carbonate (Soude) – Soda – Soda</i>	150–300 €/T
	Albite	67 % SiO ₂ , 20 % Al ₂ O ₃ , 11 % Na ₂ O, K ₂ O	Albite NaAlSi ₃ O ₈		
K ₂ O	<i>K-carbonate</i>	58 % K ₂ O, 42 % CO ₂	K ₂ CO ₃	<i>Potasa – Potasse – Potassio – Pottasche</i>	500–1500 €/T
CaO	Limestone	56 % CaO, 44 % CO ₂ , MgO, SiO ₂	Calcite CaCO ₃ , dolomite, quartz	Caliza – Calcaire – Calcare – Kalkstein	20–40 €/T
	<i>Burnt lime</i>	>98 % CaO, H ₂ O	CaO, Ca(OH) ₂	<i>Cal – Chaux – Calce – gebranntes Kalk</i>	
	Marble	56 % CaO, 44 % CO ₂ , MgO, SiO ₂	Calcite CaCO ₃ , dolomite, quartz	Marmol – Marbre – Marmo – Marmor	
MgO	Wollastonite	48 % CaO, 52 % SiO ₂	Wollastonite CaSiO ₃		80–450 €/T
	Dolomite	30 % CaO, 22 % MgO, 47 % CO ₂ , SiO ₂	Dolomite CaMg(CO ₃) ₂	Dolomie – Dolomie – Dolomia – Dolomit	20–40 €/T
	Magnesite	48 % MgO, 52 % CO ₂ , CaO	Magnesite MgCO ₃		250–400 €/T
	Talc	32 % MgO, 63 % SiO ₂ , <5 % H ₂ O	Talc Mg ₃ Si ₄ O ₁₀ (OH) ₂	Talco – Talc – Talco – Talk	100–300 €/T
	Basalt	<10 % MgO, <15 % Al ₂ O ₃ , <12 % Fe ₂ O ₃ , <12 % CaO, <44 % SiO ₂ , TiO ₂ , R ₂ O	Olivine, pyroxene, plagioclase, amphibole	Basalto – Basalte – Basalto – Basalt	10–20 €/T
Li ₂ O	<i>Li-carbonate</i>	40 % Li ₂ O, 60 % CO ₂	<i>Zabuyelite</i> Li ₂ CO ₃ , <i>Li(OH)</i> ₂		5000–5020 k €/T
	Spodumene (concentrate from pegmatite)	7 % Li ₂ O, 27 % Al ₂ O ₃ , 65 % SiO ₂	Spodumene LiAlSi ₂ O ₆ , quartz		900–1000 €/T
	Petalite (concentrate from pegmatite)	4 % Li ₂ O, 16 % Al ₂ O ₃ , 78 % SiO ₂	Petalite LiAlSi ₄ O ₁₀		800–900 €/T
B ₂ O ₃	Colemanite	50 % B ₂ O ₃ , 27 % CaO, 20 % H ₂ O, SiO ₂	Ca ₂ B ₆ O ₁₁ · 5 H ₂ O, Ca ₂ B ₆ O ₈ (OH) ₆ · 2 H ₂ O		400–600 €/T
	Ulexite	42 % B ₂ O ₃ , 13 % CaO, 35 % H ₂ O, 7 % Na ₂ O	NaCaB ₅ O ₆ (OH) ₆ · 5 H ₂ O		350–450 €/T
	<i>Borax</i>	35 % B ₂ O ₃ , 45 % H ₂ O, 15 % Na ₂ O	<i>Na₂B₄O₇ · 10 H₂O</i> , <i>Na₂B₄O₅(OH)₄ · 8 H₂O</i>	<i>Borax – Borax – Borace – Borax</i>	350–500 €/T
	<i>Boric acid</i>	56 % B ₂ O ₃ , 44 % H ₂ O	<i>Sassolite</i> H ₃ BO ₃	<i>Acido borico – Acide borique – Acido borico – Borsäure</i>	650–1000 €/T
BaO	<i>Ba-nitrate</i>	58 % BaO, 42 % NO _x	BaNO ₃		1200–1300 €/T

	<i>Ba-carbonate</i>	78 % BaO, 22 % CO ₂	<i>Witherite BaCO₃</i>		350–800 €/T
F	Fluorspar	49 % F, 72 % CaO equivalent	Fluorite CaF ₂	Fluorita – Spath Fluor – Fluorite – Flußspath	300 €/T
SO ₃	<i>Na sulphate</i>	56 % SO ₃ , 44 % Na ₂ O	<i>Thenardite Na₂SO₄</i>	<i>Sulfato – Solphate – Solfato – Sulfat</i>	100 €/T
	Gypsum	46 % SO ₃ , 32 % CaO, 21 % H ₂ O	Gypsum CaSO ₄ ·2H ₂ O	Yeso – Gypse – Gesso – Gips	10 €/T
	<i>Anhydrite</i>	59 % SO ₃ , 41 % CaO	<i>Anhydrite CaSO₄</i>	<i>Anhidrita – Anhydrite – Anidrite – Anhydrit</i>	30 €/T
Fe ₂ O ₃	Iron-oxide	>98 % Fe ₂ O ₃ , FeO	Hematite Fe ₂ O ₃ , magnetite	Hierro – Fér – Ferro – Eisen	100–2000 €/T
Cr ₂ O ₃	Chromite	68 % Cr ₂ O ₃ , 32 % FeO	Chromite FeCr ₂ O ₄ , (Fe,Mg)(Cr,Al,Fe) ₂ O ₄ magnesio-chromite – spinel solid solution	Cromita – Chromite – Cromite – Chromit	300–500 €/T
TiO ₂	Rutile	>98 % TiO ₂ , Fe ₂ O ₃	Rutile TiO ₂ , anatase, ilmenite, titanite	Rutilo – Rutile – Rutilo – Rutil	1400–1500 €/T
	Ilmenite	52 % TiO ₂ , 48 % FeO, SiO ₂	Ilmenite FeTiO ₃		150–200 €/T
ZrO ₂	Zircon	70 % ZrO ₂ , 30 % SiO ₂ , HfO ₂ , REE, Fe ₂ O ₃ , TiO ₂	Zircon ZrSiO ₄	Circón – Zircon – Zircone – Zirkon	1100–1200 €/T
P ₂ O ₅	Ca-phosphate	35 % < P ₂ O ₅ < 45 %, 35 % < CaO < 45 %, R ₂ O, H ₂ O, F	Apatite Ca ₅ (PO ₄) ₃ (OH, F, Cl)	Fosfato – Phosphate – Fosfato – Phosphat	500–1000 €/T
V ₂ O ₅	<i>Vanadium-oxide</i>	>98 % V ₂ O ₅			15,500 €/T
C	Coke	>90 % fixed-C	Coke		100–200 €/T
<i>Reducers</i>	<i>Slag</i>	30–40 % CaO, 30–40 % SiO ₂ , 10–15 % Al ₂ O ₃	<i>Glass</i>		50–200 €/T
O ₂	Cassiterite	>98 % SnO ₂	Cassiterite SnO ₂		16,000 €/T
	<i>As-oxide, As acid</i>	>98 % As ₂ O ₅			>2500 €/T
	<i>Sb-oxide</i>	>98 % Sb ₂ O ₅			
<i>Colorants</i>	<i>Se, Co, Cu, Cd, Mn</i>				

Prices only indicative as actual quotations strongly depend on quality (grain size distribution, iron content, and overall impurities), volumes, transportation costs (quarry-to-plant distance and transportation mode) and, of course, market-price fluctuations. RO = CaO and MgO; R₂O = Na₂O + K₂O.

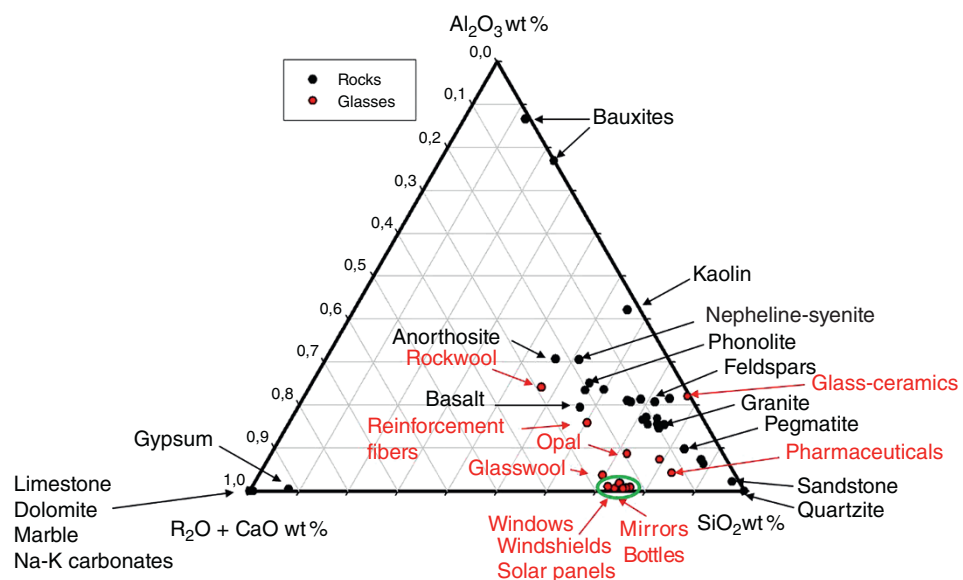


Figure 1 Comparison between the compositions of the main raw materials used in glassmaking and those of some important glass products as projected in the pseudo-ternary $\text{Al}_2\text{O}_3\text{--R}_2\text{O} + \text{CaO--SiO}_2$ diagram.

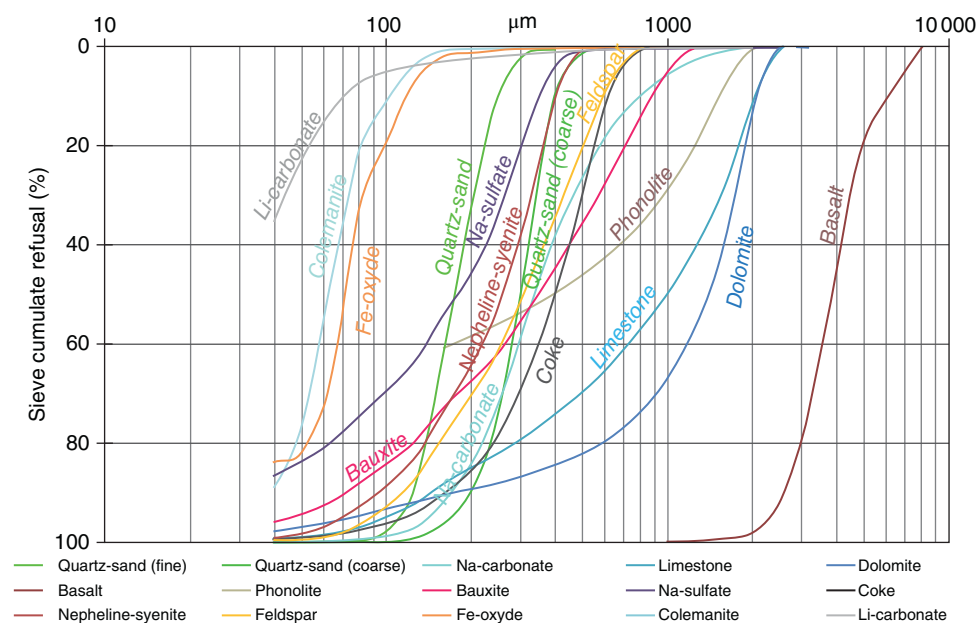


Figure 2 Sieve particle size distribution (PSD) curves of the main raw materials used in glassmaking ($<40\ \mu\text{m}$ laser PSD domain). The D50 is the median diameter representing 50% of a sieved raw material. The steeper the curve, the more homogeneous is the PSD.

2.3 Operational Parameters

Another crucial feature the glassmaker has to consider for raw-material management is the mass budget. It is common knowledge that to produce 1 ton of new, cullet-free glass, one needs around 1.2 tons of raw materials. The $\sim 20\ \text{wt}\%$ mass loss is mostly due to CO_2 released by Na, Ca, and Mg carbonates. Besides free or bound water, raw materials may in addition contain other volatile components such as unbatched carbon, fluorine, chlorine,

sulfur, or boron. When present in traces, these components are not detected through standard chemical analyses (Chapter 5.1) but can nonetheless be quantified as loss on ignition (LOI) above 1000°C . It is an important specification negotiated with the raw-material supplier since the glassmaker needs it to calculate the total mass budget of the process, including the chimney emissions that are most frequently submitted to regulatory obligations.

Because the large majority of industrial glasses are oxides, they are manufactured under oxidizing conditions. The oxygen budget is a key element to control the combustion process and, thus, melting temperatures, as well as the overall color and optical transmission of the glass, which markedly depend on redox conditions ([6], Chapter 5.6). This feature is particularly important for applications such as solar panels, and is essential for glasses made with O_2 -sensitive raw materials such as coloring agents and those that contain a significant fraction of multivalent elements.

For these reasons the glassmaker must take particular care of the total chemical oxygen demand (COD) whose proper analysis is mandatory for certain raw materials entering the batch calculation. The cullet may, for instance, contain significant amounts of organic components, such as PVC, paper, or any other residues from the downstream industrial chain. Metals, besides being detrimental to the overall quality of the glass, are oxygen sinks so that they may locally shift the overall redox budget of the process when they are oxidized. For iron as a coloring agent, for example, one cannot use iron metal, whatever its grain size, but iron oxides instead. Bearing only Fe^{3+} , hematite (Fe_2O_3) is generally selected along with magnetite [Fe_3O_4] whose mixed Fe^{3+} , Fe^{2+} valence states make it suitable for reduced compositions such as amber-glass bottles. In contrast, wüstite [FeO_{1-x}] is generally of very limited use.

Finally, the apparent density is another factor needing to be specified simply because it must be known to dimension the silos where the raw materials are stockpiled at the plant site. As an example, the bulk density of quartz is 2.65 g/cm^3 . Depending on grain shapes and contact angles, that of dry quartz sand is in contrast lower than 2 as a result of a high open porosity. Practically this means that a sand-storage silo must be at least 32% bigger than estimated from the quartz density.

3 From Raw Materials to Melt

3.1 Effects of Digestion Kinetics

The sum of the oxide contents listed in Table 1 (column “bulk chemistry”) is always lower than 100 wt %. The missing few percent mainly relate to impurities. Although it would be tempting to consider them as negligible for the overall glassmaking process, these are actually significant as illustrated by building and automotive glasses, which are manufactured with the float process (Chapter 1.3). Under standard market conditions, a float line averages 600–700 tons of daily production. This pull rate requires to introduce between 500 and 600 tons of quartz sand daily into the melter. With a SiO_2 content

of 99%, about 5 tons of impurities are then introduced at the same time. Even with an expensive 99.9% quartz, there remains about half a ton of impurities. These include different minerals, highly dispersed and diluted in the bulk, some of which may simply be incompatible with the glassmaking process because refractory materials are too slowly digested by the surrounding alkali-rich molten glass.

Even quartz does not melt during the glassmaking process, but is digested at rates of a few hundred μm per hour at 1400°C [7]. It follows that 1 mm-sized quartz grain will need hours to be completely digested. That is why raw-material suppliers sieve and sort their products, and why the maximum PSD of quartz sand is fixed at less than 1 mm by glassmakers. But dissolution rates are typically as low as a few μm per hour for commonly found heavy minerals such as corundum [$\alpha\text{-Al}_2\text{O}_3$]; zircon [$ZrSiO_4$]; kyanite, sillimanite, and andalusite [the Al_2SiO_5 polymorphs]; spinel [$MgAl_2O_4$]; and chromite [$FeCr_2O_4$]. Now, corundum, for instance, melts at above 2000°C whereas the glass temperature does not exceed 1500°C at the hottest point in a melter where the average residence time of the batch is at most a few hours. As a consequence, part of the corundum introduced as mm-sized grains would survive the glassmaking process and occurs in the final product as tiny inclusions, causing mechanical stress and impairing the optical quality. Such a product would not reach the customer to be discarded instead to the internal recycling circuit or, in the worst cases, to be dumped.

The impact of such impurities may indeed be very serious. Consider a 20 m^2 , 5-mm thick float-glass slab. With a volume of about 0.1 m^3 , its weight is 200 kg and requires 170 kg of quartz sand to be made. If on average a single mm-sized grain of chromite was present in 1 kg of the sand, then the 20 m^2 slab would display 170 dot-like defects of chromite. It would clearly be unsellable since current specifications dictate that at most one dot-like defect be present in 100 m^2 of glass. To meet glassmaking specifications, raw materials thus have to be purified by the suppliers through flotation and other costly operations [4].

3.2 Quantification of Heavy Minerals

One finds approximately 150×10^6 grains of quartz in 1 kg of fine sand [4]. In such a population it is obvious that one cannot detect one grain of chromite or other impurity by routine chemical analysis. To detect these minerals at the part-per-billion (ppb) level, one rather takes advantage of the fact that they are denser, or even much denser than quartz (e.g. corundum: $\sim 4 \text{ g/cm}^3$; chromite: $\sim 5 \text{ g/cm}^3$). One can thus concentrate them by immersing the test powder in a liquid with a density slightly higher than that

of quartz, which will then float while heavier minerals will sink, allowing the harmful ones to be identified and quantified with standard methods such as optical microscopy, Raman spectroscopy, or electron microscopy [8]. For this purpose, the most frequently used liquids have long been bromoform (CHBr_3) and diiodomethane [CH_2I_2 , also called methylene iodide], whose room-temperature densities of 2.9 and 3.3 g/cm^3 , respectively, can be slightly lowered through mixing with lighter ethanol [$\text{C}_2\text{H}_6\text{O}$]. Because strict precautions must be observed to handle these toxic liquids, however, sodium polytungstate [SPT, $3\text{Na}_2\text{WO}_4 \cdot 9\text{WO}_3 \cdot \text{H}_2\text{O}$] has become an efficient alternative [9], thanks to the fact that this salt can readily dissolve in distilled water to yield liquids with a maximum density of 3.1 g/cm^3 .

Proper sampling of raw materials [4] thus is needed to guarantee their conformity with regard to possible geological heterogeneity and product variability at the quarry level. It relies on suitable quartering techniques to obtain a true fingerprint of the mineralogy of all raw materials from which incorporation of harmful species may be ruled out or at least minimized. In other words, heavy-mineral content is an overwhelming and crucial specification concerning the physical and chemical properties that must be guaranteed by a producer of raw materials, especially when fabrication of a new glass has to be tested. Not complying with these specifications can generate long-lasting yield drops and large financial losses for the glassmaker. Since glassmakers constantly need to diversify and secure their supplies of raw materials, heavy-mineral characterization must routinely be operated by well-equipped internal or academic laboratories.

Of course, the bulk chemistry must also be determined on a daily basis at the plant by XRF, ICP-MS, or wet chemistry (cf. Chapter 5.1) to monitor the variability of moisture and oxide content, especially for multielement raw materials, and thus to allow batch adjustments needed to keep the glass recipe constant to be calculated (cf. Chapter 1.3). As indicated above, the PSD, LOI, and COD parameters must in addition be included in the almost daily control of raw materials at the plant. In this way it is possible to anticipate possible drifts away from the targeted specifications of the raw-material feed. As for the overall meltability, energy demand, and expected quality, they may be tested less routinely through differential scanning calorimetry (DSC) measurements, while it should be compulsory to test the actual batch incrementally, first in the laboratory (few kg), then in a pilot furnace (~1 ton), and finally at the industrial scale (<1000 tons).

3.3 Impurity-related and Other Melting Defects

Melting quality first and foremost depends on appropriate digestion rates. *Batch stones* can, for instance, readily

occur when market requirements push glassmakers to increase pull rates and, consequently, to reduce the average residence time of the raw materials in the furnace. They also form in case of errors in batch calculation or of scale malfunction. The problem is illustrated with the overall texture and microstructure of the silica batch stone shown in Figure 3. Noteworthy are former quartz grains, whose shape have been preserved although they have been totally replaced by cristobalite (as a pseudomorph) from which newly formed tridymite lath-shaped crystals have grown radially in a groundmass of silica glass [10]. These textural features are typical of an insufficiently dispersed quartz sand within the batch.

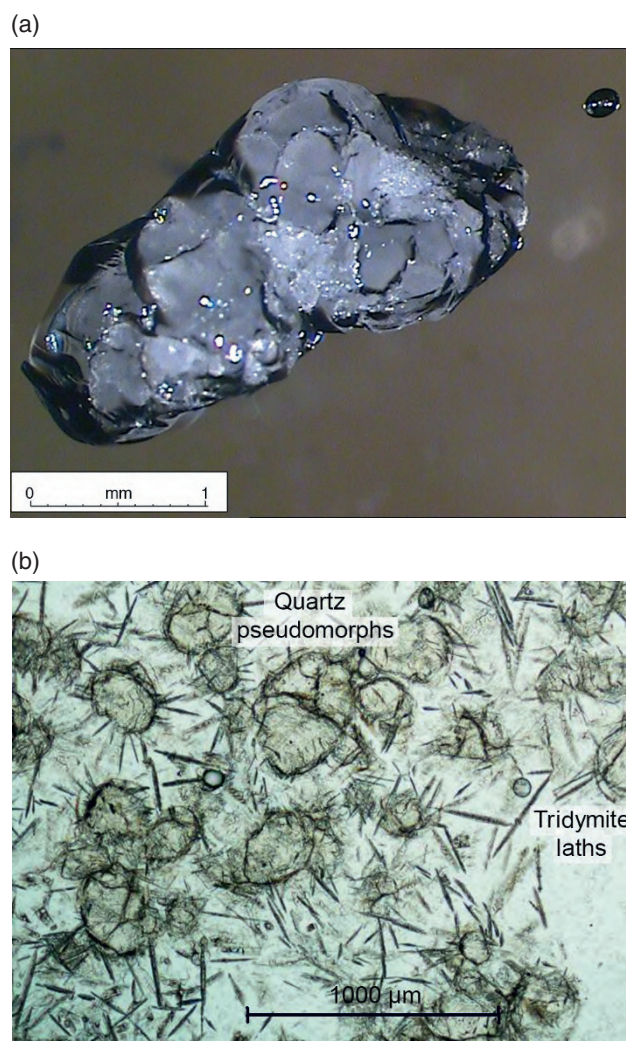


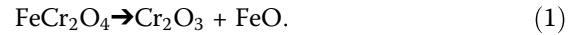
Figure 3 Silica batch stone in a soda-lime silica glass, resulting from incomplete digestion of a lump of quartz grains as viewed under an optical microscope (a) and as observed in a thin section under transmitted light (b), where rounded grains of cristobalite formed as quartz pseudomorph are sluggishly digested while generating radially growing tridymite laths in a vitreous groundmass showing an overall open-porosity.

Regardless of the actual pull rate, the overall moisture content and distribution can provoke the formation of lumps when grains stick together at the batch plant and quickly sinter at the dog-house level, preventing natural convection within the melter from properly stirring the melt under formation. Moisture is of special concern in regions facing very wet or very cold (ice) seasons. Preheating or protecting the raw materials yard can then be an effective, but somewhat costly solution.

Quartz batch stones can also result from an inadequate overall PSD when other raw materials contain up to several weight % of free silica as impurities, whose size distribution differs from that of quartz sand. Limestone, dolomite, and feldspars are typical examples, the two carbonates having a $d_{\max}$ for quartz as high as 2 mm or more

(Figure 2). Given the aforementioned digestion rates of quartz, such large grains will end up as unmolten stones in the production process.

Refractory minerals, of course, raise special difficulties as illustrated in Figure 4 by an incompletely dissolved chromite inclusion. Its core is preserved as FeCr_2O_4 , but it is surrounded by newly formed laths of eskolaite [Cr_2O_3] radially growing from it according to the decomposition reaction:



Although Fe^{2+} then diffuses in the melt, the highly refractory eskolaite crystals (melting at 2435°C) passivate the chromite core, which will thus remain throughout the production process.

Incomplete digestion can alternatively cause the existence of vitreous inclusions called *knots* in the glassmaker jargon. The example shown in Figure 5 is that of an mm-sized pocket of alumina-rich glass within the normal soda-lime silica matrix, which represents the ghost of a feldspar crystal. As already stated, feldspar minerals melt at temperature below 1200°C , therefore early in the process, i.e. already at the dog-house level. When they do so, they generate an alumina-rich liquid phase whose viscosity of 10^5 dPa s at 1000°C is 10 times higher than that of the soda-lime silica glass [11]. At high pull rates this difference prevents rapid enough interdiffusion from taking place to ensure complete mixing between the two liquids, whence the presence of knots. A simple solution to avoid them when Al-carriers are feldspars thus is to control the PSD of these minerals. But, with very different PSD ranges, feldspars can also be present as impurities in a variety of materials such as quartz-sand, limestone, and dolomite. Likewise, a proper

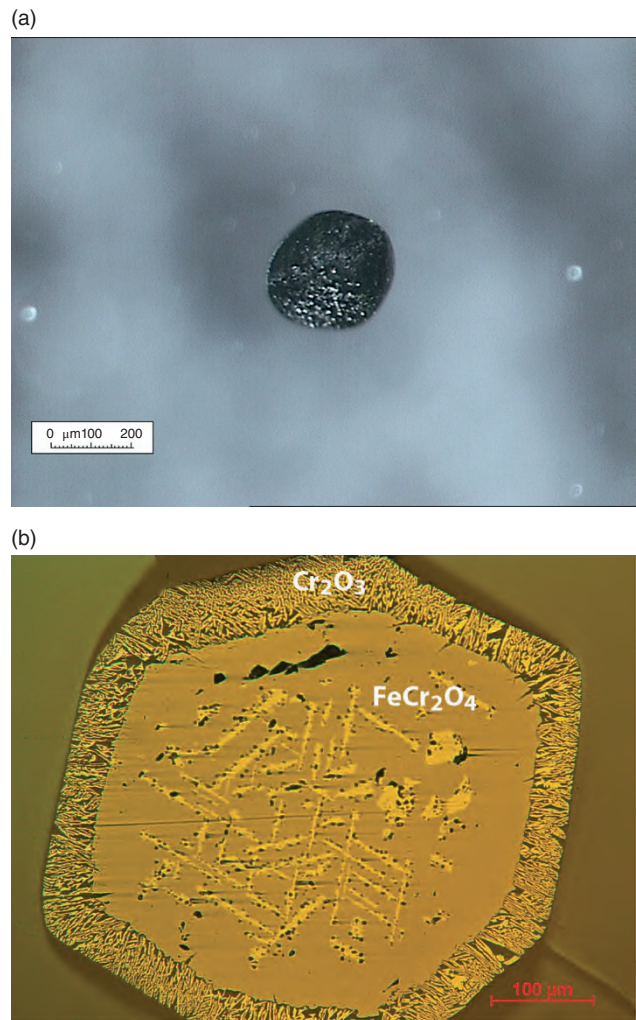


Figure 4 Undissolved chromite crystal in a soda-lime silica glass as seen under a binocular microscope (a) and in a polished thin section photo under reflected light (b). The chromite grain shows a preserved FeCr_2O_4 core, exsolution lamellae, and radially growing eskolaite Cr_2O_3 laths in the outer shell.

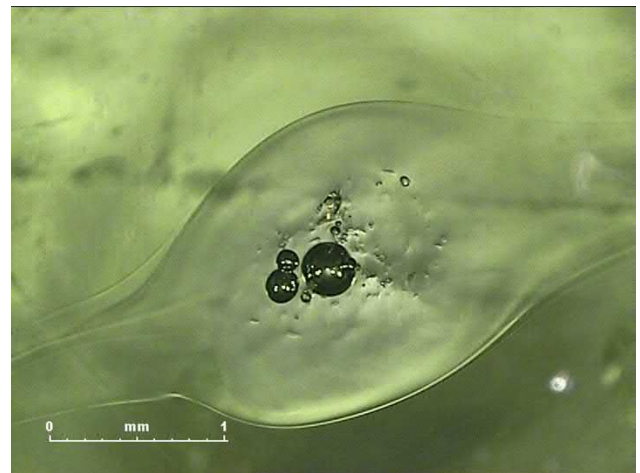
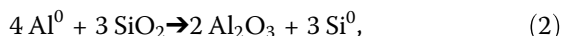


Figure 5 A feldspar knot with about 20 wt % Al_2O_3 , enclosing bubbles (gas inclusions) in a soda-lime silica glass as seen under a binocular microscope.

PSD helps minimizing the presence of alumina-rich knots in the final product when the Al-rich phonolite and nepheline syenite rocks are used as raw materials.

Even cullet may be a source of defects, which has important practical consequences since it accounts for up to 80–90 % of the total batch for tinted soda-lime silica glasses used for packaging, and up to 30 % for standard-window and windshield glass production. In this case, the culprit is metallic aluminum from soda-drink cans that pollutes household cullet or from framework residues of window cullet coming from building demolishing sites [10]. Through the redox reaction [12]



metallic silicon forms while hydrogen is liberated by the reduction of OH-group from the glass network. The result is a sub-mm-sized silicon bead surrounded by H₂-rich gas inclusions (Figure 6), which are virtually indestructible because they are digested at rates of the order of a few μm per hour. Appropriate cullet management is thus needed to reduce this risk in glass production. For similar reasons, the absence of ceramic, porcelain, and glass-ceramic shards polluting the external cullet must also be checked carefully to avoid stones, knots, and slowing down of the production.

Another special case arises from the presence of nickel in raw materials. In sulfate-fined glasses, reduction of NiO yields nickel metal, which can react with trace amounts of sulfur to form small inclusions of NiS [mill-erite] [13]. The problem here is that this sulphide in principle undergoes near 390 °C a phase change from a high-temperature α-polymorph to a denser low-temperature β-polymorph. The kinetics are slow



Figure 6 A sub-mm-sized silicon bead surrounded by H₂-rich gas inclusions in a soda-lime silica glass, resulting from aluminum-metal contamination of recycled cullet.

enough, however, that the phase transition can take place at room temperature several days to several months or even years after tempering (Chapter 3.12). When it eventually does so, the 2–4% volume expansion generates cracking and sometimes the explosion of the finished glass product. Hence, both Ni metal and oxides are nowadays proscribed in raw-material specifications.

3.4 The Problem of Dolomite Decrepitation

Even when all chemical, physical, and mineralogical specifications are respected, some raw materials may pose special difficulties upon heating. Decrepitation is such a special case affecting mainly dolomite [14] and, albeit to a lesser extent, limestone. It occurs at 300–400 °C, hence well before the onset of decarbonation and decomposition of the (Ca, Mg) carbonate. Although it is still poorly understood [14], decrepitation appears to result from a sudden change in the overall PSD of dolomite, and an overall increase of fines, when dolomite grains locally burst into smaller grains. The decrepitation factor is defined as the increment in the fraction of grains smaller than 60 μm after heating at 1000 °C. It can range from a few to several 10% depending on geological history and, in particular, on the thermal pathway followed by the dolomite after its formation. High-decrepitation dolomites are detrimental to the glass process because they contribute to further increase in dust and carryover in the furnace atmosphere. The latter in turn contribute to clogging phenomena at the level of regenerator chambers, drastically decreasing their energy-recovery efficiency. Furthermore, dolomite dusts may increase the overall wear of the furnace-superstructure refractories through the formation of new Mg-bearing phases that decrease their overall durability. When a local supply of good-quality dolomite is lacking, glassmakers may thus find safer to produce Mg-free glass.

4 Special Raw Materials

4.1 Sodium Carbonate

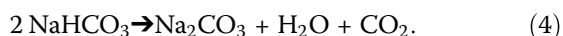
Originally known as natron, sodium carbonate hydrates have been the main flux used ever since the beginnings of glassmaking. As exemplified by the celebrated Wadi el Natroun deposits in Egypt (Chapter 10.3), very pure Na₂CO₃ hydrates did form naturally but such deposits currently satisfy only about 30 % of 50 million tons used annually in industry, half of which for glassmaking. The cheapest source of sodium would be NaCl, but this salt is quite unfit for production of oxidized glasses in view of chlorinated emissions that would in particular dramatically degrade the wearing resistance of the furnace

refractories. Soda [NaOH] would be a much better alternative, but its price on an Na₂O basis is twice that of synthetic Na₂CO₃ as manufactured with the Solvay process [15], which currently supplies 59% of the market.

Sodium is most conveniently added to the batch as Na₂CO₃, whereas CaCO₃ is the most common source of carbonate ions. Hence, the goal of the Solvay process is to achieve the overall reaction:



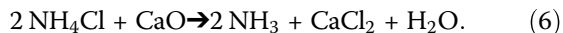
Now, this reaction could not proceed directly in the solid state even if its Gibbs free energy of about 100 kJ/mol were not positive. But Na₂CO₃ is readily obtained through heating of NaHCO₃ precipitates at around 200 °C:



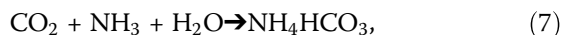
The trick of the Solvay process thus is to produce sodium bicarbonate in an aqueous solution from an NaCl brine with the reaction



which, as a by-product, yields calcium chloride, a valuable compound:



The first step then consists in producing a solution of ammonium bicarbonate with



such that NH₃ and CO₂ are in the end “totally” recycled within the process.

4.2 Raw Materials with Very Low Iron Contents

Given its strong absorption bands (Chapter 6.2), iron badly needs to be present at the lowest possible concentrations in a variety of glasses for which optical transmission must be optimized. This is, for instance, the case of the sheets protecting silicon wafers from oxidation in solar panels or of the mirrors used for concentrating solar energy in thermal solar plants. Such solar glasses are currently the most transparent available on the market with an optical transmission that can be as high as 91–92%, against values lower than 90 % for standard glasses used in windows or car windshields. Although it might appear small, this difference is in practice significant so that it is worth the subsequent increases in the cost of the raw materials. Here, two factors must be considered, namely the total iron content and the iron redox state. Whereas the latter can be controlled through various process parameters, the former is, of course, determined by the batch

composition. Specifically, the total iron content of extra-clear glasses for solar applications must be below 100 ppm [16], compared to the 600–1000 ppm of clear glass for windows. Natural raw materials with so low iron contents are rare, however, so that suppliers need beneficiation processes to reach them [4]. Grinding then becomes an issue because of potential iron contamination by the steel of the machines. Magnetic separation then is a convenient way to remove any added iron as the last step of raw-material preparation (Figure 7).

4.3 Globetrotting Raw Materials

Like other capital-intensive activities, glassmaking plants traditionally are local industries so as to minimize transportation costs of both raw materials and finished products. Although not necessarily rare geologically, however, certain minerals are not commonly found in commercially exploitable amounts with the consequence that they have to be procured globally, national policies sometimes applying heavy, protectionist custom fees to limit exportations. This situation applies, for instance, to lithium, boron, and some aluminum carriers.

In glassmaking, lithium occasionally serves as an additive (flux) for the production of standard soda-lime silica glasses, but it is mainly used for glass-ceramics to form the β -spodumene [LiAlSi₂O₆] phase that gives them very low thermal expansion coefficients (Chapter 7.11). But the price of Li₂O raw materials has been boosted – it has actually almost tripled – during the last decade, driven by the dramatically increasing demand for Li-ion batteries (Chapter 9.5). Among the available Li₂O raw materials (Table 1), Li from brines is mostly used to manufacture Li-carbonate or hydroxide (battery-grade raw materials), whereas mineral Li is incorporated into glass and ceramics. Concentrates of both minerals, spodumene and petalite, are actually crucial sources for the glass industry [17, 18], which does not require as high a purity as Li-ion battery makers. These Li-silicate sources are abundantly available in Australia, China, the United States, and Canada, but much rarer and mostly unexploited in Europe (Austria, Finland, Ireland, Portugal, and Spain) where most of the glass-ceramic industries are in fact located.

As for boron, this element is important for the production of reinforcement fibers (Chapter 1.5) and for insulation (Chapter 9.3) and textile glasses. Borates are found in Turkey, the United States, China, Russia, and South America. Turkey is the world's biggest producer and holds the largest reserves. The United States ranks second both in terms of reserves production, with about 40% of the market [19]. In this case too, the heterogeneous distribution of boron sources translates into high transportation costs as a component of the raw-material supplies.

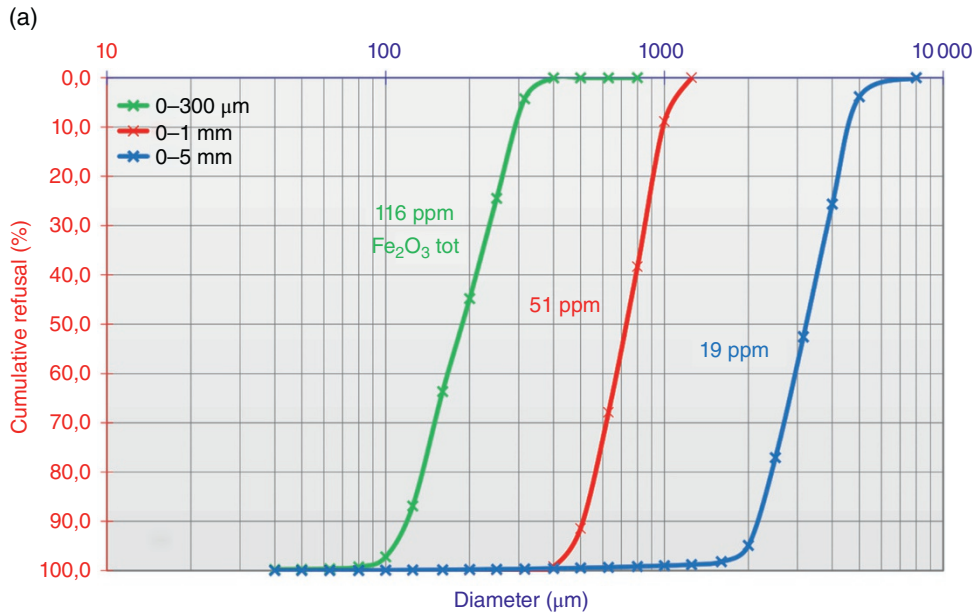


Figure 7 Increases of iron contamination caused by grinding of quartz made with steel-bearing jaws to shift the particle size distribution. (a) Iron contents associated with the PSD curves of quartz sand and flour ground. (b) Alignment of steel particles in the magnetic field of the separator during the deferrization step of raw-material beneficiation. Picture scale of 0.5 m.

Concerning aluminum, bauxites and laterites are used as Al-carrier in standard industrial glasses. The main and largest exploited ores, representing more than 90% of the reserves, are located in Western Africa (especially Guinea), Brazil, Central America and the Caribbean (Jamaica, Trinidad and Tobago, Suriname) and Australia [20]. In this market, however, glassmakers are very distant followers of alumina-ceramics makers and especially of metallic aluminum producers whose needs are several orders of magnitude higher than theirs. In instances when relatively high contents of both aluminum and alkalis are required, it may be advantageous to use instead nepheline

syenite, a rock consisting mainly of alkali feldspars and nepheline $[\text{NaAlSiO}_4]$, which is exploited and exported from Norway, Russia (Kola Peninsula), South-Africa, Brazil, India, and China.

5 Perspectives

More than 100 million tons of glass (container, flat, fiber, and specialty) are produced yearly. In a society moving toward a CO₂-less or -free economy, extra-clear glasses

will play a key role for the development of an efficient solar energy market. As the availability of extra-pure raw materials is not infinite [16], however, beneficiation techniques will need to be improved in order to meet cost-efficient requirements adapted to the forthcoming societal challenges. In terms of both volumes and quality, middle- and long-term availability of raw materials is a major challenge for sustainable, cost-related production. But a successful low-carbon society implies the fast development of infrastructures and commodity products, which contribute to the overall industrial minerals' demand in direct competition with the glass raw materials supply chain [16]. Governmental initiatives, such as the European Union ERA-MIN Program [21] and the EIT Raw Materials, intend to build an EU-wide network linking industry, academia, and research institutes capable of sustaining the domestic supply chain of non-energy mineral resources. In parallel, efforts are made to improve batch recipes through either the use of standard raw materials with lower energy consumption [22], or totally new ways exploiting the huge potential of the recycling supply chain. Food and agriculture wastes, for instance, could allow making glass with "exotic" sources such as eggshells for Ca-carbonate, banana peels as K-carrier, or rice husk for silica [23]. Major changes are likely on the way.

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1.3

Fusion of Glass

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1 Introduction

Fusion is of course the high-temperature process through which a glass is synthesized from the relevant raw materials. In this chapter, fusion and melting will be used synonymously as no preference for either term obtains in glass manufacturing. Nevertheless, the matter deserves a few comments because both are used to describe different processes under conditions of constant pressure. They may denote:

- 1) A first-order phase transition of a single-component system (such as pure H_2O , SiO_2 , or $\text{CaAl}_2\text{Si}_2\text{O}_8$) from the solid to the liquid state. This transition occurs at a unique melting (or fusion) temperature T_m where the solid and liquid coexist; between them, however, there exist discontinuities in enthalpy and entropy, which are the enthalpy (ΔH_m) and entropy ($\Delta S_m = \Delta H_m/T_m$) of melting (or of fusion).
- 2) The transition of a thermodynamically stable assemblage of different crystalline phases to the liquid state. Upon heating, such a system passes through a temperature range at which the solid and liquid phases coexist; the solidus (T_{sol}) and liquidus (T_{liq}) temperatures are the lower and upper bounds, respectively, of this interval.
- 3) The transition of any mixture of crystalline phases to the liquid state upon heating. Since such phases are not in thermodynamic equilibrium, they begin to react mutually in the solid state so that the actual path of fusion may be unpredictably complicated.
- 4) A special technique, often used by artists, to join pieces of glass together to form an object. It makes use of the fact that a glass, upon heating, undergoes gradual softening from a rigid condition below the

glass transition temperature T_g to the liquid state at $T > T_g$. At sufficiently high temperatures, glass pieces may then be joined together by viscous flow. The transition from a crystalline state is here nonexistent, which distinguishes clearly this special meaning of *fusion* from the three others.

In glassmaking, it is of course case (3) that matters, which is why it will be exclusively dealt with in this chapter. It begins with the heating of a mixture of granular solids, the *batch*, and is completed when a homogeneous liquid state is reached. Regardless of the complexity of its chemical composition, any glass is associated with a liquidus and a solidus temperature between which crystals and melt can coexist in thermodynamic equilibrium. Upon not too fast heating, a liquid for instance begins to form at the liquidus temperature of the system as determined by its overall chemical composition.

At the industrial scale, the fusion of glass is a most complex energy-intensive, high-temperature process. The transformations involved in are multiphase, multicomponent chemical reactions, which are quite different from a student's simple concept of chemical reaction. The goal of the fusion process consists in delivering a workable glass melt of high quality at high production rates and low specific-energy consumption, thereby abiding with environmental legislation. It brings together the issues of reactor technology, bulk solid melting, particle dissolution, as well as redox and acid–base chemistry of the melt. Fusion takes place in specifically designed glass furnaces. Small amounts of specialty glass are melted discontinuously in crucible, pot, or day tank furnaces; the melting compartments may be considered as crucibles of different size, ranging from a few kg to a few 100 kg. For continuous melting of small amounts of some specialty glasses, rotary kilns are used. But the vast majority of glasses is

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continuously melted in large glass furnaces whose production capacities range from a few tons to 1000 t per day.

Regardless of this diversity, fusion involves the same steps that will be successively described in this chapter. The first is the careful preparation of the batch from the appropriate raw materials. The second takes place at high temperatures through the various reactions that lead to a melt through complete dissolution of even the most refractory starting materials. The third step aims at producing a homogenous, bubble-free product by physical and chemical fining. Finally, this chapter will briefly discuss the economically and environmentally important energetics of the fusion process. A review of earlier work dealing with these issues is the feature article by Cable [1].

2 Overview of Industrial Processes

A continuously operated industrial melting process can be split into two distinct room- and high-temperature parts within which well-defined different steps may generally be identified. Their main features are as follows:

Preparation (at room temperature)

P1	Acquisition and storage of raw materials
P2	Chemical analysis of raw materials
P3	Calculation of the proportions of the batch raw materials
P4	Weighing and then mixing of the batch raw materials
P5	Intermediate storage of the batch in a buffer silo
P6	Batch charging

Glass melting (at high temperatures)

M1	Primary batch-to-melt conversion, yielding a <i>rough melt</i> still containing considerable amounts of gas bubbles and undissolved solids Time demand: about one hour Intrinsic energy demand: about 2000 MJ/t of produced glass (3.6 GJ = 1 kWh) Temperature range: 600–1200 °C
M2	Sand dissolution (comprising the dissolution of any other crystalline solids) Temperature range: 1200–1400 °C Intrinsic energy demand (mostly for heating up the melt): approx. 280 MJ/t of glass
M3	Fining, i.e. physical removal of residual bubbles via the thermochemical generation of an adequately high-volume fraction of large bubbles of a fining gas Temperature range: 1400–1500 °C Intrinsic energy demand (for heating-up): approx. 140 MJ

M4	Refining, thermal, and chemical homogenization, whereby refining denotes the resorption of residual gas bubbles upon steady cooling Target temperature: 1350 °C Heat released: –220 MJ.
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At the end of step M4, the melt is finally conveyed to the forming area where it is transformed into hollow ware (Chapter 1.5), or flat glass (Chapter 1.4), or any other type of product. To maintain a high glass quality, the filling level of the melting compartment must be kept constant. Therefore, the sequence of process steps P1 to M4 must be well balanced logistically. This constraint puts a stringent time interval to act for online corrections to steps P4–P6; the buffer silo between steps P5 and P6 thus serves the sole purpose of widening this interval. Along the path from P6 to M4, no action for correction is possible at all.

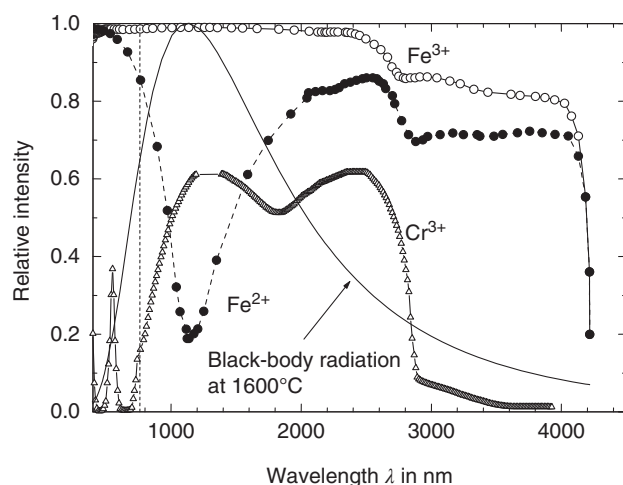
3 Batch Preparation

3.1 Raw Materials

The fusion of a glass of a given composition requires a suitable set of raw materials (Chapter 1.2). These are selected according to their availability and quality, which, in turn, determine their price. The issue of availability may be complex since it includes geological occurrence (for natural materials), production capacity (for manufactured materials), infrastructure for recycling and upgrading (for cullet) as well as transport distance, number of tenders, political stability at the source, etc. Quality is likewise a manifold issue as it concerns chemical composition (from impurities to the main component), mineralogical composition (special attention being paid to side minerals difficult to melt), and grain size distribution (with a particular concern to under- and oversized grain fractions). Among chemical impurities, iron is a critical factor. It is present in virtually every natural raw material but is generally tolerated in glass only at very low levels (Table 1) except, of course, when it is itself a major component of the product as in fire-resistant glass fibers (Chapter 9.3). Here, the iron content is given in terms of stoichiometric Fe_2O_3 irrespective of its actual valence state. Yet, iron is generally present as Fe^{2+} and Fe^{3+} whose relative abundances depend on the redox state of the melt. Owing to the strong absorption bands of both cations, iron has a strong impact on the color of the glass even at low concentrations (Chapter 6.2). And because of its strong absorption in the 600–4000 μm wavelength range, which is that of the heat radiation in the furnace, Fe^{2+} acts as a blinding agent to limit tightly the

Table 1 Maximum iron contents in various types of glasses, given in ppm of stoichiometric ferric iron (Fe_2O_3).

Glass type	ppm Fe_2O_3
Optical glass	10
Ultra-white glass	100
Continuous fibers	200
Flint container glass	250
Standard float glass	300
Amber container glass	2 500
Cr-green container glass	10 000

**Figure 1** Absorption bands of Fe^{2+} , Fe^{3+} , and Cr^{3+} in a glass melt, and radiation intensity in the combustion space of a furnace illustrated in a simplified way by black-body radiation emitted at 1600°C from the upper lining (the crown) of the furnace; relative intensities.

transparency of the melt to IR radiation (Figure 1). In Figure 1, the furnace radiation is illustrated by a black-body-type curve. This is an oversimplification. The actual flame radiation spectrum in a furnace is characterized by strong emission lines of the H_2O and CO_2 molecules in the flame (H_2O : $0.9\text{--}1.1$, $1.8\text{--}2.0$, $2.5\text{--}3.2\ \mu\text{m}$; CO_2 : $2.7\text{--}3.0$, $4.2\text{--}4.7\ \mu\text{m}$) and by black-body radiation from soot particles. The radiation enters the melt directly to a certain extent; however, chiefly via emission (emission coefficient $\varepsilon \approx 0.5$) and diffuse reflection from the top lining (the crown) of the furnace. The curve shown in Figure 1 is an envelope of the actual radiation only. Irrespective of the above details, furnaces in which glasses with high Fe^{2+} contents are melted thus exhibit large vertical temperature gradients and low bottom temperatures; heat transfer from the combustion space has then to be brought about by the convective motion of

the melt. By contrast, melts with very low amounts of Fe^{2+} weakly absorb energy from the combustion space since Fe^{3+} does not influence IR absorption. As a consequence, they display high temperatures at the bottom of furnaces. Controlling the redox state of the melt thus is important not only for color generation but also for furnace operation, a general conclusion that also applies for instance to green glasses colored by Cr^{3+} .

3.2 Calculation of Batch Composition

An accurate chemical analysis of every raw material is a prerequisite for batch preparation (Chapter 1.2). On this basis, one swiftly determines the batch composition by solving a system of linear equations where data are arranged in a specific way (Table 2). First, the total number of different oxides in the raw material basis is determined (6 in the example shown). The target glass composition is entered as an oxide column vector Y_{TARGET} . The large matrix shaded in gray contains the results of raw-material analyses. It is arranged in the order of carriers of the respective glass oxides. For each oxide that is not represented by a specific raw material, the entry 1 is filled in the matrix. If an oxide has more than one carrier raw material (in the example, Al_2O_3 has two carriers, namely feldspar and Calumite®), then their ratio has to be specified, and the respective column entries are merged to a single column in proportion of this ratio. Through these operations, the gray area takes the form of a square matrix M . Next, a preliminary vector R_{PRE} of the batch composition is obtained from the product $R_{\text{PRE}} = M^{-1} \cdot Y_{\text{TARGET}}$. It may contain negative figures since it is impossible to make for example an iron-free glass from iron-containing raw materials. To derive the actual batch-composition vector R , these negative figures are thus set to zero. The real glass composition is then given by the product $Y_{\text{REAL}} = M \cdot R$ before Y_{REAL} is normalized to 100 wt % and R to 1000 kg of resulting glass, or 2000 kg of sand (see following paragraph), or to any other convenient reference mass.

Final adjustment of the batch composition still requires allotments of the appropriate agents for controlling glass color, fining (as described in Section 5.2), redox conditions, and, thus, valence states and oxygen complex formation of polyvalent ions (cf. Chapter 5.6) at the industrial scale. For adjustment of the redox state, the so-called redox number concept [2] is widely accepted and empirically applied in industry. This incremental system assigns a specific redox factor R_i to every member of a set of redox-active ingredients i (Table 3). In the example of Table 4, the batch composition from Table 2 is complemented by 4 kg of sulphate (the amount of soda ash being reduced accordingly to maintain an identical amount of Na_2O in the glass). Then the batch

Table 2 Batch calculation scheme.

The glass			The raw material basis									
			Raw material	Sand	None	Feldspar	Calumite®	None	Dolomite	Limestone	Soda ash	None
			For oxide	SiO ₂	TiO ₂	Al ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O
			Ratio			0.5	0.5					
Y _{TARGET}	Y _{REAL}											
Oxide	wt %	wt %	Oxide	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg
SiO ₂	72.00	71.80	SiO ₂	0.9960		0.6920	0.3550		0.0002	0.0040		
TiO ₂	0.00	0.04	TiO ₂	0.0001	1.0000		0.0080					
Al ₂ O ₃	1.50	1.50	Al ₂ O ₃	0.0009		0.2010	0.1250					
Fe ₂ O ₃	0.00	0.03	Fe ₂ O ₃	0.0002			0.0020	1.0000		0.0007		
MgO	3.00	2.99	MgO				0.0650		0.2160	0.0057		
CaO	9.50	9.47	CaO				0.4090		0.3070	0.5502		
Na ₂ O	14.00	13.96	Na ₂ O			0.0620	0.0170				0.5868	
K ₂ O	0.00	0.21	K ₂ O			0.0370	0.0110					1.0000
Sum	100.00	100.00	Sum	0.9972	1.0000	0.9920	0.9920	1.0000	0.5232	0.5606	0.5868	1.0000
			Batch composition vector R in kg raw material per t of glass.									
			kg/t	674.28	0.00	44.02	44.02	0.00	123.39	70.61	231.99	0.00

The results of the considered raw-material analysis is reported in the shaded gray area of the matrix.

Table 3 Redox factors $R(i)$ of selected active raw materials i ; these factors refer to batch compositions normalized to a sand amount of 2000 kg.

Raw material i	Chemical formula	$R(i)$ per 2000 kg sand
Carbon	C : 100, 85, 65%	-6.70
Iron sulfide	FeS	-1.60
Pyrite	FeS ₂	-1.20
Fluorspar	CaF ₂	-0.10
Calumite	Multicomponent slag	-0.073
Iron red	Fe ₂ O ₃	+0.25
Chili saltpeter	NaNO ₃	+0.32
Heavy spar	BaSO ₄	+0.40
Gypsum	CaSO ₄ ·2 H ₂ O	+0.56
Potassium dichromate	K ₂ Cr ₂ O ₇	+0.65
Salt cake; sulfate	Na ₂ SO ₄	+0.67
Gypsum anhydrite	CaSO ₄	+0.70
Sodium dichromate	Na ₂ Cr ₂ O ₇	+0.77
Manganese oxide	MnO ₂	+1.09

composition is normalized to amounts $m_{III}(i)$ per 2000 kg of sand, and the total redox number of the batch is calculated from the weighted sum $R = \sum R_i \cdot m_{III}(i)$. It is true that this number R does not have a straightforward scientific meaning but it allows one to set in a well-defined way the redox state to a desired level. For redox numbers in the

interval $-25 < R < 25$, a fair estimate of the Fe^{2+}/Fe_{total} ratio for is given by $0.4 - 0.015 \cdot R$. Because the chemical composition of the batch can no longer be corrected after charging, these rather simple calculations are mandatory for any successful melting process.

Finally, the raw materials are automatically weighed in proportions determined by batch calculations, conveyed to a mixer, and thoroughly mixed. During mixing, typically 2–3% of water is added to suppress dust formation and segregation induced either originally by transportation or subsequently by mixing. In batches containing soda ash, small amounts of this product dissolve in the water before reprecipitating on other batch grains. This process termed “impregnation” actually enhances the kinetics of batch melting.

4 The Conversion of Batch into Melt

4.1 The Basic Importance of Convection

In principle, the melting compartment (the *tank*) is a shallow basin whose typical dimensions (length $L \times$ width $W \times$ depth D) are $10 \times 6 \times 1 \text{ m}^3$ for medium-size container-glass furnaces and $30 \times 10 \times 1.4 \text{ m}^3$ for float-glass furnaces. The required energy is delivered in a combustion space right above the melting compartment and transferred to the melt chiefly by black-body radiation. Additional energy (5–20%) is delivered by direct electrical heating (*boosting*) of the melt.

The very melting process, i.e. steps M1–M3, takes place in one single box-shaped compartment as sketched in Figure 2a, b. The sketches illustrate some essential

Table 4 Scheme for final batch adjustment with sodium sulphate set to 4 kg/t glass for a targeted redox number R of -24.

Raw material i	$m_i(i)^a$	$m_{II}(i)^b$	$m_{III}(i)^c$	$R(i)$	$R(i) \cdot m_{III}(i)$
	kg/t glass	kg/t glass	kg/2000 kg sand		
Sand	674.28	674.28	2000.00		
Feldspar	44.02	44.02	130.57		
Calumite	44.02	44.02	130.57	-0.073	-9.53
Dolomite	123.39	123.39	365.99		
Limestone	70.61	70.61	209.44		
Soda ash	231.99	229.01	679.26		
Sulfate		4.00	11.86	0.67	7.95
Carbon		1.13	3.35	-6.70	-22.46
Redox number $R = \sum R_i \cdot m_{III}(i)$					-24.04

$\sum R_i \cdot m_{III}(i)$ matches the target value $R = -24$.

^a Batch composition as calculated in Table 2.

^b Batch composition with 4 kg of sulfate added, soda ash reduced accordingly.

^c Batch composition normalized to 2000 kg of sand; amount of carbon varied until the sum.

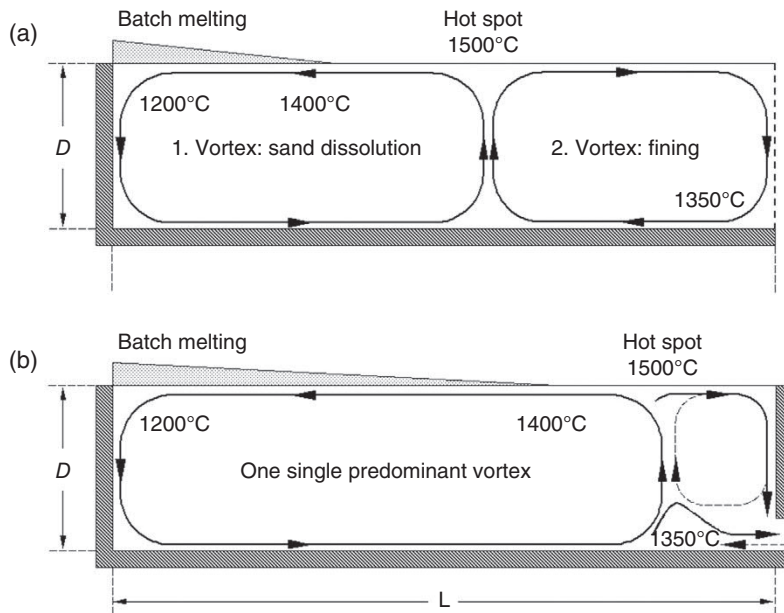


Figure 2 Convection cells (vortices) in the melting tank of a glass furnace (vertical projection): (a) float glass furnace (side port firing), transit to the refining zone indicated by the dotted vertical line on the right-hand side; (b) end port fired container glass furnace, transit to the refiner through a narrow opening at the lower right (the “throat”); D = depth of the tank.

features only (see Chapter 9.7 for details). Spatially, the individual process steps are separated – not in a rigorous but effective way – by two convective vortices. In furnaces with transversal flame direction (so-called side port fired furnaces; flow pattern Figure 2a), these are mainly generated thermally by an appropriate distribution of fuel input to a series of burners arranged along the L axis above the melt. This results in two well-developed vortices with a well-localized hot spot at the position of maximum energy input. In furnaces with longitudinal flame direction (end port fired furnaces; flow pattern Figure 2b), the energy input via combustion along the L axis cannot be controlled at the same distinction as in a side port fired furnace. Here, the flow pattern is typically dominated by a single predominant vortex; the hot spot is shifted toward the end of the furnace. Local stabilization of the vortices is achieved by electrical heating from below, and – for the second type of furnaces – also mechanically by the action of air bubblers or by implementation of a solid barrier (a *wall*) at the bottom of the tank. As seen from Figure 2, the batch floats on the surface of the molten phase and melts continuously in the L direction, thereby typically covering an area whose length is about $L/3$, or more than $2L/3$ for side and end port firing, respectively. Processes M2 (sand dissolution) and M3 (fining) then take place in the first and second vortices, respectively. Note that the first vortex conveys very hot melt right underneath the batch, helping to satisfy the very high intrinsic energy demand of melting. As for the second, it transports a very hot (hence low-viscosity) melt along the surface area, thereby facilitating the escape of rising bubbles. This effect is especially pronounced in the pattern shown in

Figure 2a while in Figure 2b, a large portion of the melt does not reach the surface at all.

At a given pull rate p in t/h, the nominal overall dwell time of the melt in the furnace is

$$\tau_{\text{NOM}} = \rho L W D / p \quad (1)$$

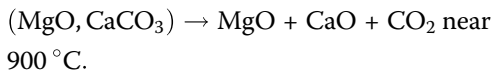
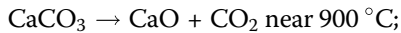
where ρ is the density of the melt and $L \cdot W \cdot D$ the volume of the melting tank. Depending on the size of the furnace and the targeted glass quality (in terms of residual bubbles), τ_{NOM} ranges from 20 to 40 hours. During this time, the average volume element circles 2–6 times in vortex 1, and about twice in vortex 2. For a detailed analysis of the role of the flow pattern on melting and fining, see [3, 4]. The process of refining (M4) already starts at the descent of vortex 2; it is completed in a subsequent compartment termed *refiner*, which is thermally separated from the *melter*. Thermal separation is accomplished either with a vertical wall leaving an opening of about $0.5 \times 0.3 \text{ m}^2$ cross section (the *throat*) at half width right above the bottom of container-glass furnaces (Chapter 1.5), or by an area of moderately narrowed width (the *waist*) in float glass furnaces (Chapter 1.4). For the sake of glass quality (i.e. homogeneity), it is mandatory to keep the position of the hot spot constant at any pull rate.

4.2 The Chemistry of Melting

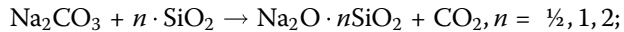
The first high-temperature process is primary melting of the batch. It is typically accomplished within one hour and is characterized by a very high energy demand and

the release of CO_2 from the carbonated raw materials. For a glass batch, the individual reactions involved are the following ones:

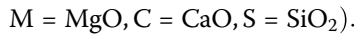
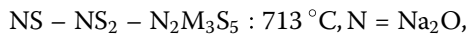
- 1) *Physical melting of salt-like raw materials*, Na_2CO_3 , Na_2SO_4 , NaNO_3 , NaOH , NaCl , etc.
- 2) *Evaporation of batch and hydrate water* in the temperature range $100\text{--}600^\circ\text{C}$.
- 3) *Decomposition of limestone and dolomite*:



- 4) *Formation of a double carbonate*: $\text{Na}_2\text{CO}_3 + \text{CaCO}_3 \rightarrow \text{Na}_2\text{Ca}(\text{CO}_3)_2$ near 785°C ; in conventional batches, this is a side reaction of only minor importance.
- 5) *Formation of silicate melts*. These reactions assume noticeable turnover rates only after actual melting of soda ash:



Formation of ternary melts (eutectic $\text{NS--NS}_2\text{--N}_2\text{CS}_3$: 821°C , eutectic



- 6) *Sulphate coal reaction*: $\text{Na}_2\text{SO}_4 + 4\text{CO} \rightarrow \text{Na}_2\text{S} + 4\text{CO}_2$ at approx. 900°C .

- 7) *Reactions with cullet*. Although it appears as a neutral post in the energy balance, cullet vigorously react with soda ash; very fine cullet compete with sand for soda ash, delaying sand dissolution.

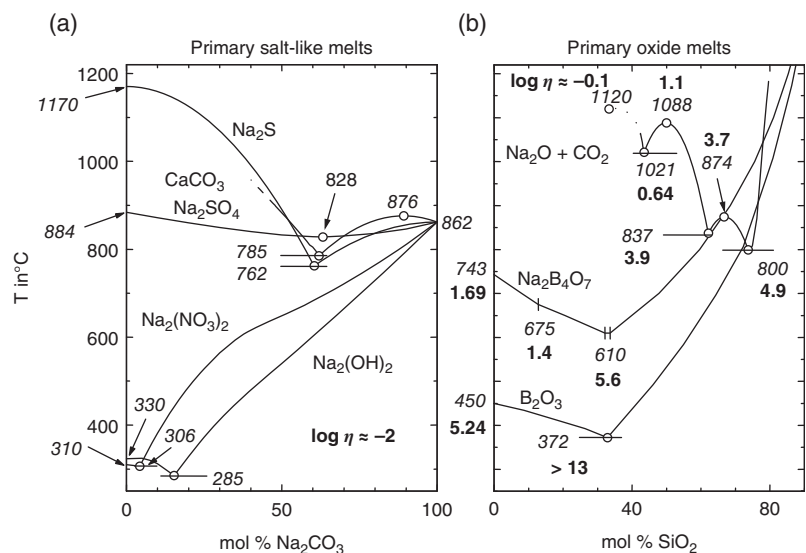
The liquidus temperatures and viscosities of the primary melts forming during the early stages of batch melting are plotted in Figure 3 in the cases of binary salt-like melts formed from soda ash and another compound (Figure 3a) and of the systems $\text{Na}_2\text{O--SiO}_2$, $\text{Na}_2\text{B}_4\text{O}_7\text{--SiO}_2$, and $\text{B}_2\text{O}_3\text{--SiO}_2$ (Figure 3b).

Owing to their extremely low viscosities, the salt-like primary melts play an important role in bringing about high turnover rates during batch melting. When they are lacking, as in alkali and boron-free continuous fiber glasses, the products in contrast remain in a granular state until they reach their lowest eutectic temperature (compare with Figure 6b in Chapter 6.1).

These different stages of early batch melting are sketched in Figure 4 for a soda lime silicate glass batch. Before a soda-ash melt forms, the batch remains in a granular state (Figure 4a). Then, a primary salt-like, low-viscosity melt rapidly spreads throughout the batch, thereby wetting the solid grains (Figure 4b). This stage is characterized by a large ratio between the liquid interface and the melt volume. It is predominantly at this time that diffusion paths for oxygen exchange are short and that the surrounding atmosphere effectively interacts with the melt to determine its final redox state.

Upon further melting (Figure 4c, d), the melt becomes increasingly viscous and the ratio of liquid interface to melt volume decreases. In a real batch heap, stages (a) to (d) proceed longitudinally along the L axis (see Figure 2) and vertically from the outside to the inside of the batch. The batch melts from both its top and

Figure 3 Liquidus temperatures and viscosities (dPa·s) of primary melts formed during the early stages of batch melting. (a) Binary salt-like melts formed from soda ash and another compound. (b) Primary oxide melts in the systems $\text{Na}_2\text{O--SiO}_2$, $\text{Na}_2\text{B}_4\text{O}_7\text{--SiO}_2$, and $\text{B}_2\text{O}_3\text{--SiO}_2$. Invariant points indicated by open circles.



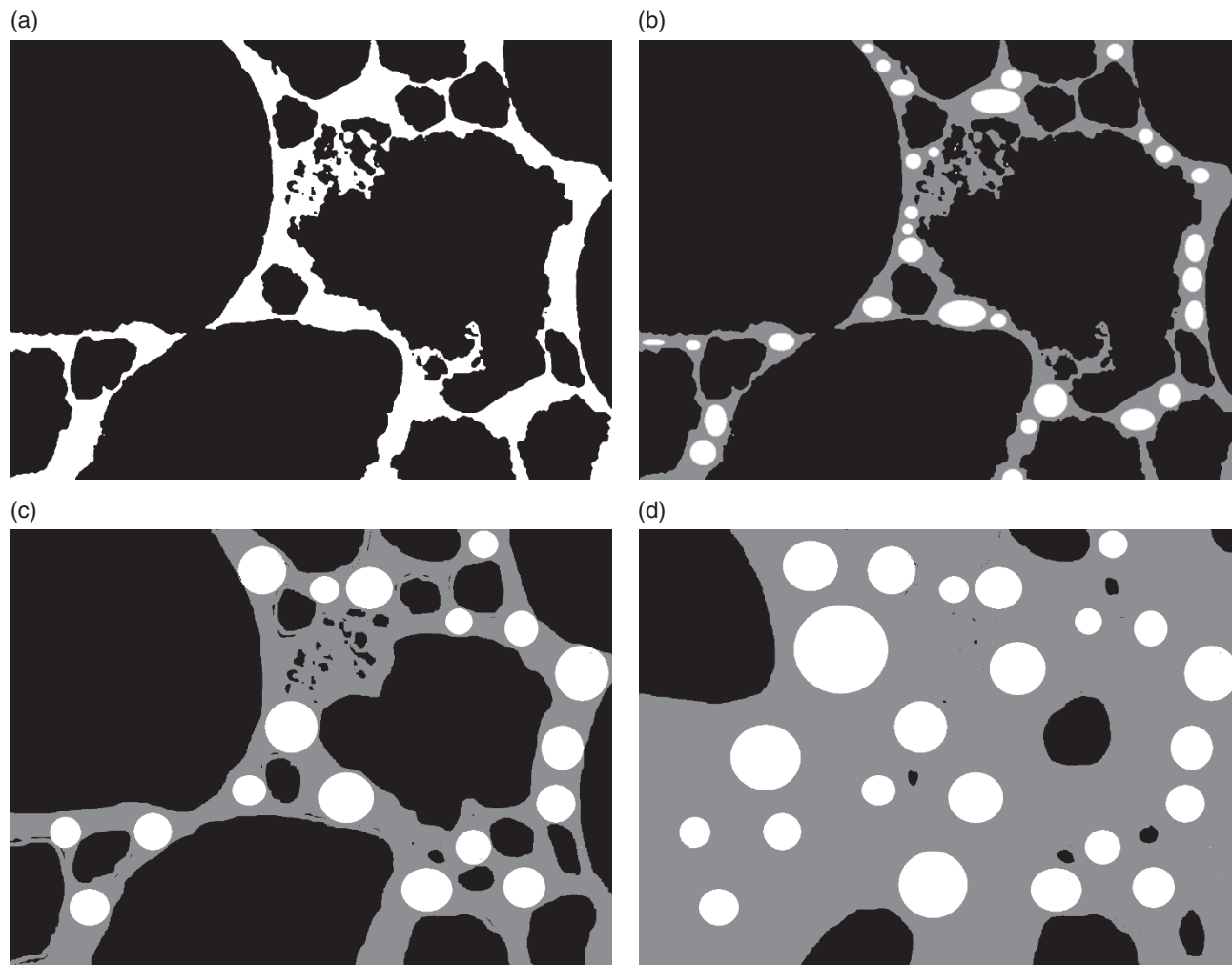


Figure 4 Early stages of batch melting, manually sketched after the scanning electron microscopy micrograph. (a) Open-pore stage with granular solids and gas, the gas composition being dominated by the equilibrium between CO_2 and O_2 from trapped air and the furnace atmosphere. (b) Closed-pore stage with the development of a widespread primary liquid, a large ratio s of effective liquid interface (solid/liquid and solid/gas) and liquid volume, and a gas composition dominated by CO_2 , redox active materials, and polyvalent ions in the primary melt. (c) Reaction-foam stage characterized by large volumes of granular solids, bubbles, and melt, and by progressive melting of solids and decreasing s ratios. (d) Rough-melt stage, the melt being the predominant phase coexisting with considerable amounts of bubbles and undissolved grains and showing on top a seam of the primary foam formed.

bottom side, typically in an almost symmetrical way as the heat fluxes from above and below are of the same order of magnitude. The release of gases is in contrast asymmetric since those from the upper parts readily escape whereas those coming from the lower parts remain trapped below the batch. In a successful primary melting process, the majority of solids are digested, only a minor part being released to the rough melt. This requires good batch mixing and a well-balanced granulometry of the raw materials. The issue can be tested at the lab scale by so-called batch-free time crucible tests. In these simple tests, batch samples of 50–100 g are exposed to a laboratory furnace at 1400°C and the progress of melting is inspected visually after a given time.

4.3 Sand Dissolution

All solids surviving primary batch melting have to dissolve in the viscous rough melt by slow diffusion processes under comparatively low driving chemical forces. This is one of the reasons why, even today, long dwell times are required for the fusion process. By mass, the sand represents the major part of solids that have to dissolve in this way. The process suffers from an especially unfavorable feature (Figure 5): the decrease of the silica concentration from the sand grain to the melt phase represents a strong chemical gradient that causes the grain to be surrounded by a seam of melt with a high viscosity and a low basicity. This gradient affects not only

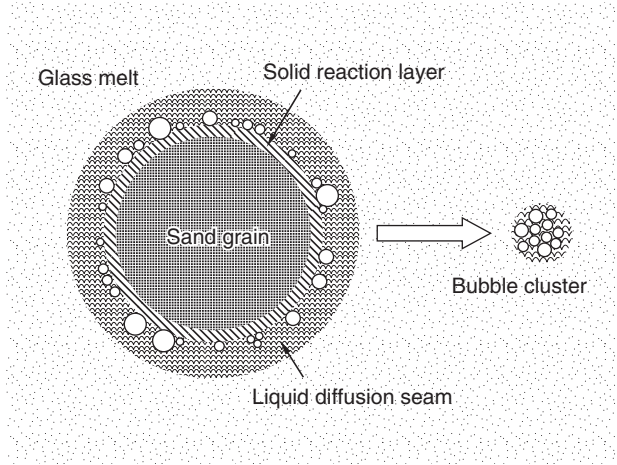
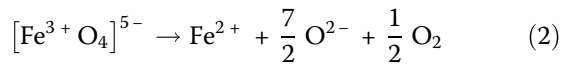


Figure 5 Schematic view of a dissolving sand grain; the grain is surrounded by a solid reaction layer (e.g. tridymite) followed by a liquid high-viscosity diffusion seam with decreasing SiO_2 concentration, hence decreasing acidity, from inside to outside; gas bubbles – mostly O_2 – precipitate at the interface solid/liquid; upon complete dissolution of the sand grain, a bubble cluster remains in the melt.

mass transport but also the solubility of gases, which generally decreases with decreasing basicity (cf. Chapter 5.7). Thus, gases dissolved in the rough melt tend to form bubbles around a dissolving sand grain.

In addition, temperature-induced reduction of ferric iron takes place as described by the reaction



describing how firm $[\text{Fe}^{3+}\text{O}_4]$ oxygen complexes give rise to the weak $[\text{Fe}^{2+}\text{O}_6]$ complexes formed by ferrous iron. The equilibrium constant of the reaction is given by

$$K_p = \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \cdot [\text{O}^{2-}]^{7/2} \cdot P(\text{O}_2)^{1/2} \quad (3)$$

so that, at constant redox state, tiny oxygen bubbles emerge at the boundary of the dissolving grain. Any dissolving sand grain leaves behind it a cluster of small bubbles, removal of these bubbles makes sense only if their generation is over. This is one of the reasons why sand dissolution and the fining process need to take place in separate parts of the furnace.

In summary, successful sand dissolution is a prerequisite for successful fining. Even apparently small differences in the grain-size distributions of sands have a big impact in this respect. This statement will be demonstrated for two different sands. Let us assume that a spherical sand grain with radius r dissolves according to Jander's kinetics:

$$\alpha(r, t) = 1 - \left(1 - \sqrt{\frac{t}{t^*(r)}}\right)^3, \quad t^*(r) = \frac{r^2}{4 \cdot D}. \quad (4)$$

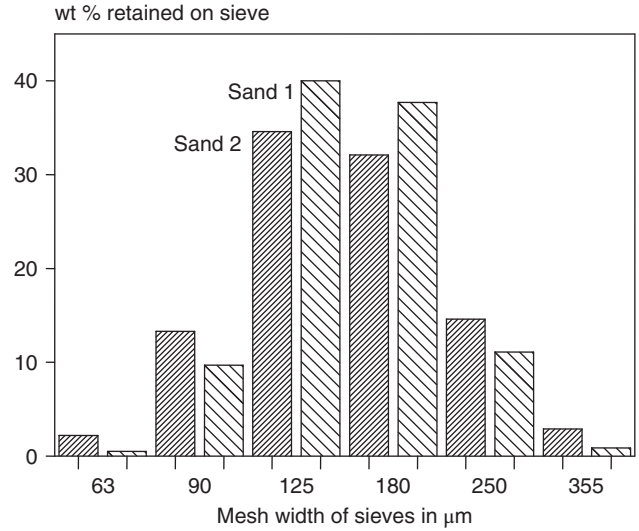


Figure 6 Grain-size distributions of two different glass-grade sand qualities as determined with sieves of increasing mesh width.

Here, $\alpha(r, t)$ denotes the turnover, with $0 \leq \alpha(r, t) \leq 1$ and D a diffusion coefficient. The grain-size distribution is mathematically represented by a log-normal distribution, the differential form of which reads

$$q(r) = \frac{1}{\sqrt{2\pi} \cdot \sigma \cdot r} \cdot \exp \left[- \left(\frac{1}{\sqrt{2} \cdot \sigma} \cdot \ln \frac{r}{r_{50}} \right)^2 \right], \quad (5)$$

where r_{50} is the median radius of the particle size distribution and $\sigma = \frac{1}{2} \cdot \ln(r_{84}/r_{16})$ is the standard deviation denoting the width of the distribution; 16 and 84% by mass of the sand are contained in the fraction smaller than r_{16} and r_{84} , respectively. The values of r_{50} and σ are determined by an evaluation of the sieve analysis (Figure 6). Both sand qualities have an identical median $d_{50} = 2 \cdot r_{50} = 180 \mu\text{m}$, but different σ . An ensemble of grains with a size distribution $q(r)$ then dissolves according to the equation

$$A(t) = \int_0^{r=\sqrt{4Dt}} q(r) dr + \int_{r=\sqrt{4Dt}}^{\infty} \alpha(r, t) q(r) dr \quad (6)$$

where $0 \leq A(t) \leq 1$ denotes the reaction turnover of the entire ensemble. The results for the two selected sand qualities upon isothermal dissolution are shown in Figure 7 as obtained with the solution of Eq. (18) given in the Appendix. At first sight, both kinds of sands dissolve in about the same manner. But on closer

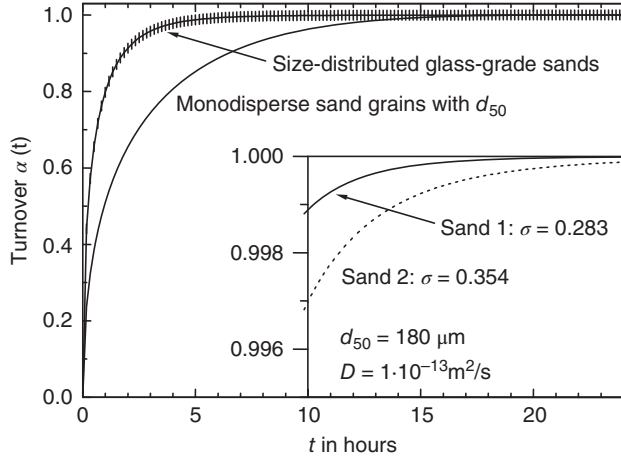


Figure 7 Dissolution turnover of the two sands of Figure 6 as a function of process time for isothermal diffusion with $D = 1 \cdot 10^{-13} \text{ m}^2/\text{s}$. Inset: magnification of the results for nearly complete dissolution.

inspection (see inset), the difference does become large toward the very end of the process since Sand 2 needs significantly many more hours than Sand 1 to reach a 99.9% dissolution level, which is crucial for glass quality.

5 Fining, Refining, Homogenization

5.1 Physical Fining

As noted above, the ideal onset of fining takes place when sand dissolution is complete. Physically, fining relies on two simultaneous processes, namely bubble removal by buoyancy and coalescence of small bubbles to form larger ones. The latter is driven by the release of energy associated with the excess internal pressure of a bubble relative to ambient. As given by Laplace's formula, this excess pressure is $\Delta P = 2\sigma/r$ for a bubble of radius r with a surface tension σ so that the energy gained amounts to about $3.5 \cdot \sigma \cdot r$ when two bubbles of identical size merge. As for the buoyancy velocity v_0 of a single bubble in a melt of viscosity η , it is given by a modification of Stokes' law for dispersed phases with mobile boundaries known as Hadamard's law:

$$v_0 = \Delta \rho g r^2 / 3\eta, \quad (7)$$

where g is the gravitation constant and $\Delta \rho$ the density difference between the melt and bubble.

For a melt with a volume fraction ϕ of bubbles, the effective viscosity becomes

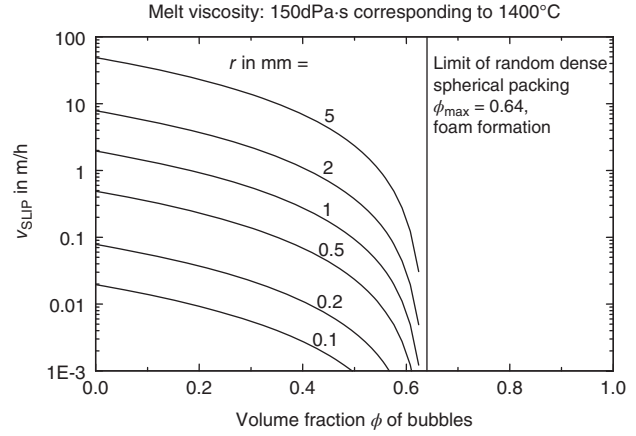


Figure 8 Rising velocity v_{SLIP} of bubble swarms in a melt at a viscosity of 150 dPa·s as a function of bubble radius r and volume fraction ϕ of bubbles.

$$\eta_{\text{eff}} = \eta (1 - \phi / \phi_{\text{max}}) \quad (8)$$

where $\phi_{\text{max}} = 0.64$ is the maximum value of ϕ as given by random close spherical packing. But the density decrease caused by the presence of bubbles, which is proportional to $1 - \phi / \phi_{\text{max}}$, must also be taken into account. The rising velocity v_{SLIP} of an individual bubble within a bubble swarm of volume fraction ϕ thus is

$$v_{\text{SLIP}} = v_0 \eta / \eta_{\text{eff}} = \Delta \rho g r^2 / 3\eta (1 - \phi / \phi_{\text{max}})^2. \quad (9)$$

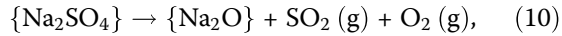
The situation is illustrated in Figure 8 for a viscosity of 150 dPa·s, which is that of a typical float glass melt near 1400 °C. Up to a volume fraction of 0.4, bubbles bigger than 0.5 mm in radius safely escape during the available process time, whereas those smaller than 0.1 mm hardly reach any noticeable rising velocity. They rather rest relative to the environment. An especially critical situation occurs when the volume fraction approaches the limit ϕ_{max} . In this case, bubbles of any size become stagnant so that a foam forms on top of the melt in the fining area as observed in a glass of beer. Hence, this problem calls for utmost care in the design of the chemical part of the fining process, and especially of the amount of fining agent used.

5.2 Chemical Fining

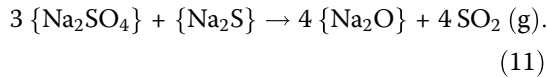
As indicated by old glass specimens, bubbles cannot be completely eliminated with only physical fining. In a somewhat paradoxical way, better results are achieved if additional bubbles are produced within the melt at a sufficiently high, yet not too high, volume fraction to coalesce with the bubbles formed or entrapped during

melting. The process is known as *chemical fining* as it involves reactions with gas-releasing substances.

For reasons of cost, chemical compatibility, and effectiveness, the most widely used agent is sodium sulphate (Na_2SO_4). By experience, 4 kg of Na_2SO_4 are added per ton of produced glass. During the early stages of batch melting, the sulfate dissolves in the melt. Under oxidizing conditions, it decomposes at 1400–1450 °C according to the reaction



where the braces $\{-\}$ denote the state “dissolved in the melt.” Under reducing conditions, sodium sulphate reacts with the Na_2S formed during primary batch melting as follows:

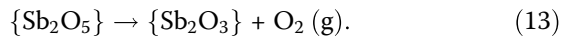


The latter reaction already occurs at temperatures slightly below 1400 °C.

Oxygen fining is an alternative option. The agent typically used is Sb_2O_3 ; it is added to the batch in amounts of 3–5 kg per 1000 kg of sand, in combination with a four- to eightfold amount of NaNO_3 [5]. At the moderately low temperatures of primary batch melting, Sb_2O_3 converts to $\{\text{Sb}_2\text{O}_5\}$ provided that a sufficiently high oxygen partial pressure in the batch is established (Figure 4, stage b). This is achieved by the action of NaNO_3 , which decomposes at batch melting temperatures to release oxygen:



At increasing temperatures, the higher valences of polyvalent ions become increasingly unstable (see Chapter 5.6) so that the fining reaction actually reads



The release of oxygen bubbles reaches its maximum at about 1300 °C and extends beyond 1400 °C. The negative side effect of this procedure is the formation of the NO_x pollutant.

A simple calculation will finally explain why experience and empirical knowledge still play the predominant role in the allotment of fining agents. As used in the batch in Table 4, a mass of 4 kg of Na_2SO_4 represents 56.3 mol of SO_2 , which, at 1400 °C, 1 bar, would fill a volume of 7.6 m³. Now, 1 ton of melt, by contrast, fills 0.4 m³ only. Obviously, only a very minor part of the nominal SO_2 ends up in gas bubbles otherwise a foam instead of a clear melt would be obtained. The major part of SO_2 is in fact lost during batch melting, by evaporation from the melt surface, or is retained in the glass. Thus, the proper

allotment of fining rests on the small difference between sulfate input and the above losses. One of the rare attempts to perform a detailed sulfur balance of a glass furnace revealed that approximately 0.25–0.3 kg of the sulfate added per t of glass are released in the form of fining bubbles [6].

5.3 Homogeneization

After the fining process, the melt is cooled down and homogenized thermally in a steady way. Small residual bubbles resorb themselves because the solubilities of most volatile species strongly decrease with increasing temperatures (Chapter 5.5). For this reason, care has to be taken to prevent local temperature rises from happening during the homogenization process otherwise the so-called *reboil bubbles* would form in the melt and could not be removed in any way. Among dissolved gases, N_2 distinguishes itself by its decreasing solubility with decreasing temperatures. Thus, N_2 -containing bubbles escaping the fining process appear as very tiny bubbles called *seeds* in the final glass. Their number per unit mass of glass represents an important quality criterion. In container glass, a few tens of seeds per 100 g of glass are accepted. Float glass requires a much higher quality (one visible defect per 20 m² already is considered a high defect density) and hence, much longer dwell times (approx. 1.5–2 days vs. 1 day for container glass) in the melting compartment.

6 Energetics of Glass Melting

The amount of energy involved in the fusion of glass is an issue of great interest to the glass industry. Referring to comprehensive quantitative treatments ([7, 8] and Chapter 9.8), we will give only a brief sketch of this issue within the scope of this chapter. The approach rests on the fact that, at constant pressure, the heat (enthalpy) transferred to or drawn from a system is thermodynamically the variation of a state function: as such, the intrinsic energy demand depends only on the initial and final states of the system and it can be determined without any consideration of what is going on along the process road.

The initial enthalpy state is given by the sum of standard enthalpies H°_i at 25 °C, 1 bar, of the individual raw materials i , weighted by their respective amounts m_i in the batch:

$$H^\circ_{\text{BATCH}} = \sum m_i \cdot H^\circ_i. \quad (14)$$

The final enthalpy is given by the standard enthalpies of the batch gases g , $H^\circ_{\text{GASES}} = \sum m_g \cdot H^\circ_g$, and of the glass,

H°_{GLASS} , plus the heat content $\Delta H(T_{\text{ex}})$ of the glass at the exit temperature T_{ex} . The standard enthalpy difference between inputs and products constitutes the chemical energy demand

$$\Delta H^\circ_{\text{chem}} = H^\circ_{\text{BATCH}} - H^\circ_{\text{GASES}} - H^\circ_{\text{GLASS}}. \quad (15)$$

The heat content of the melt at T_{ex} is given by $\Delta H(T_{\text{ex}})$. For convenience, all enthalpy values are inserted in absolute figures, disregarding the minus sign given in thermochemical tables. The overall intrinsic heat demand H_{ex} (exploited heat of the process) is given by

$$H_{\text{ex}} = (1 - y_{\text{CULLET}}) \cdot \Delta H^\circ_{\text{chem}} + \Delta H(T_{\text{ex}}), \quad (16)$$

where y_{CULLET} denotes the weight fraction of cullet per amount of glass produced.

It is true, real raw materials typically do not contain their main mineral phase only, but also contain minor amounts of side minerals. For example, a real quartz sand may contain, beside its main phase quartz, minor amounts of feldspar minerals, magnetite, spinel, etc.; a natural dolomite is typically composed of different minerals forming solid solutions in the system Ca–Mg–Fe^{II}–CO₃ with an overall composition not too far from the pure phase CaMg(CO₃)₂. An accurate determination of the enthalpy values H°_i of real raw materials would thus require the evaluation of multicomponent phase diagrams. However, such an approach would hardly be accepted by the technological community. Beyond this, the gain of accuracy against a simpler approach is minor only. Thus, with the reservation to a more rigorous treatment [7, 8], only the enthalpy values H°_i of pure raw materials are given here in units of MJ/kg:

Raw material <i>i</i>	Enthalpy H°_i in MJ/kg
Pure quartz sand	15.150
Pure albite (NaAlSi ₃ O ₈)	14.952
Pure dolomite CaMg(CO ₃) ₂	12.549
Pure calcite CaCO ₃	12.058
Soda ash	10.659
Sodium sulfate	9.782
Carbon	0.000
Calumite®	13.561

For the batch gases, the following values hold:

CO₂: 8.941; H₂O: 13.422; SO₂: 4.633; O₂: 0.000.

The energy calculation for the real glass composition of Table 2 (where the tiny amount of TiO₂ has been allotted to SiO₂) is summarized in Table 5. The position of the

glass composition in the phase diagram in units of kg of equilibrium compounds per t of glass is found by the following simplified procedure:

$$\begin{aligned} \text{NAS}_6 &= 51.440 \text{ Al}_2\text{O}_3 - 55.697 \text{ K}_2\text{O}, \\ \text{KAS}_6 &= 59.102 \text{ K}_2\text{O}, \\ \text{hm} &= 6 \text{ Fe}_2\text{O}_3, \\ \text{FS} &= 7.345 \text{ Fe}_2\text{O}_3, \\ \text{MS} &= 24.907 \text{ MgO}, \\ \text{NC}_3\text{S}_6 &= 35.112 \text{ CaO}, \\ \text{NS}_2 &= 29.386 \text{ Na}_2\text{O} + 19.346 \text{ K}_2\text{O} - 17.867 \text{ Al}_2\text{O}_3 \\ &- 10.824 \text{ CaO}, \\ \text{S} &= \text{difference to 1000 kg}. \end{aligned}$$

Oxide amounts are to be inserted in wt %. For the components *k*, the shorthand notation hm = FeO·Fe₂O₃, F = Fe₂O₃, M = MgO, C = CaO, N = Na₂O, K = K₂O, S = SiO₂ is used. Column m(*k*) in Table 5 lists the resulting amounts of the constitutional components of the glass. By this procedure, one finds that the standard enthalpies of formation of the glass and melt are 14 189.7 MJ/t at room temperature and 12 665.9 MJ/t at 1300 °C, respectively. The enthalpy physically stored in the melt at 1300 °C relative to the glass at 25 °C is thus 1523.8 MJ/t. By the weighted sum of the heat capacity of compounds *k*, the latter value can be adjusted to any other exit temperature of the melt. For the batch given in Table 4, column “*m_{II}(i)*”, a chemical energy demand of $\Delta H^\circ_{\text{chem}} = 461.8$ MJ/t is obtained. Fusion of the selected batch with 50% cullet ($y_{\text{CULLET}} = 0.5$) thus requires an intrinsic energy demand of

$$\begin{aligned} H_{\text{ex}} &= (1 - y_{\text{CULLET}}) \cdot \Delta H^\circ_{\text{chem}} + \Delta H(T_{\text{ex}}) \\ &= 1745.7 \text{ MJ/t}. \end{aligned} \quad (17)$$

A well-constructed and operated melting furnace (end port, air-gas fired) reaches an efficiency of heat exploitation η_{ex} of 48%. Thus, the actual energy demand H_{in} of the melting process amounts to $H_{\text{in}} = H_{\text{ex}}/\eta_{\text{ex}} = 3637$ MJ/t. This result is very much in line with industrial experience. Calculations of this kind are of high importance for the evaluation of glass furnace performance [9], for furnace design, as well as for the energy optimization of batch and glass compositions.

7 Perspectives

Although the energetics of the fusion process may be considered as satisfactorily assessed, the kinetic aspects of fusion are not yet well enough understood. The efficiency of heat exploitation η_{ex} of a furnace varies according to a hyperbolic law of the type $\eta_{\text{ex}} = 1/(A + B \cdot p)$ with the production rate *p* (t/h). Thus, furnaces are preferentially operated at the highest achievable rates. The limits for *p* are determined by the rate of heat transfer or the time

Table 5 Calculation scheme for the energetics of a soda-lime silicate glass (composition in wt %).^a

Oxide	wt %	Compound <i>k</i>	$H^\circ_{k, \text{GL}}$	$H_{k, 1300}$	$c_{p, k, L}$	$m(k)$	$m(k) \cdot H^\circ_{k, \text{GL}}$	$m(k) \cdot H_{k, 1300}$
			MJ/kg	MJ/kg	kJ/kg·K	kg/t	MJ/kg	MJ/kg
SiO ₂	71.84	hm	4.4313	3.0196	0.9217	0.18	0.8	0.5
Al ₂ O ₃	1.50	FS	8.7888	7.3999	1.0589	0.22	1.9	1.6
Fe ₂ O ₃	0.03	MS	14.9599	13.2740	1.4582	74.47	1114.1	988.5
MgO	2.99	NS ₂	13.4194	11.6862	1.4335	284.99	3824.4	3330.4
CaO	9.47	NC ₃ S ₆	14.0278	12.6137	1.3301	332.51	4664.4	4194.2
Na ₂ O	13.96	NAS ₆	14.7131	13.2234	1.2358	65.46	963.2	865.6
K ₂ O	0.21	KAS ₆	14.0258	12.5775	1.3755	12.41	174.1	156.1
Sum	100.00	S	15.0023	13.6179	1.4347	229.75	3446.9	3128.8
						Sum	H°_{GLASS}	$H_{1300, \text{MELT}}$
						1000.00	14 189.7	12 665.9
							ΔH_{1300}	
							1523.8	

^a $H^\circ_{k, \text{GL}}$ = standard enthalpy of component *k* in the glassy state; $H_{k, 1300}$ = enthalpy of *k* in the liquid state at 1300 °C; $c_{p, k, L}$ = isobaric heat capacity of liquid *k*; $m(k)$ = equilibrium amount of *k* in the multicomponent phase diagram; H°_{GLASS} = standard enthalpy of the resulting glass;

$H_{1300, \text{MELT}}$ = enthalpy of the melt at 1300 °C; ΔH_{1300} = heat content of the melt at 1300 °C relative to the glass at 25 °C.

^b hm = FeO·Fe₂O₃, F = Fe₂O₃, M = MgO, C = CaO, N = Na₂O, K = K₂O, S = SiO₂.

demand of the fusion process required to achieve an acceptable glass quality. As of now, however, one does not even know which of the above constraints controls the melting rate. As a matter of fact, the answer depends on both furnace and batch design.

A better understanding of redox and acid base reactions in real furnaces is also desired. Although these reactions are well understood at the laboratory scale, the transfer to a real production situation is still set by experience rather than by scientific principles. In view of the large impact of these reactions on glass quality, progress in this area would be highly appreciated.

Finally, the glass industry is engaged in a quest to lower its overall energy consumption to decrease its operating costs and to satisfy increasingly stringent legislation imposed on high-temperature industrial processes. The design of faster conversion batches is becoming important in this respect. Conventional glass formulae and batch recipes are no longer taken for granted. Efforts are in particular made to design batches that would melt along reaction pathways ensuring higher turnover rates than current randomly mixed batches. Progress may be achieved with selective batching, granulation processes bringing the reaction partners into close contact at the μm scale, preparation of core-shell type pellets, or selective preheating of specific raw-material combinations of the batch. In each case, of course, a prerequisite would be that the obtained energy savings are not offset by increased batch costs.

Appendix

The results plotted in Figure 7 for the dissolution of an ensemble of grains have been obtained from the analytical solution to the integral $A(t)$ of Eq. (6) given by:

$$\begin{aligned}
 A(t) = 1 - \frac{1}{2} \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y\right) + \frac{3y}{2} \cdot \exp\left(\frac{s^2}{4}\right) \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y + \frac{s}{2}\right) \\
 - \frac{3y^2}{2} \cdot \exp(s^2) \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y + s\right) \\
 + \frac{y^3}{2} \cdot \exp\left(\frac{9s^2}{4}\right) \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y + \frac{3s}{2}\right), \\
 y = \frac{\sqrt{4 \cdot D \cdot t}}{r_{50}}, \quad s = \sqrt{2} \cdot \sigma
 \end{aligned}
 \tag{18}$$

Here, $\operatorname{erfc}(z)$ denotes the complementary Gaussian error function of argument z , while y and s are used as abbreviations in the formula. It is true that sand dissolution does not proceed isothermally at a constant diffusion coefficient D in a real fusion process, but the utmost importance of the grain-size distribution for a successful fusion process is nonetheless demonstrated clearly.

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1.4

Primary Fabrication of Flat Glass

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1 Introduction

Flat glass is ubiquitous in the modern world, from the facades of high-rise buildings to the large windows of automobiles, the solar power generation systems, and the various kinds of displays that are now integral components of daily life. Not only did these new applications cause a tremendous increase of the world production from less than 7×10^5 in the early 1960s to 59×10^6 metric tons in 2014 (then with an annual growth rate of 7%), but they have also yielded dramatic improvements in glass quality and functionalities. For a glass material that had been manufactured for 2000 years with very little change, the industrial evolution observed during the last 50 years has been incredibly rapid indeed!

As experienced by ancient Roman glassmakers, flat glass made by pouring the melt on a solid substrate has a surface that is not smooth enough to ensure good transparency. Until the beginning of the twentieth century, flat glass had for this reason to be produced out of hollow glass to keep the defect-free surface conferred by fire polish. As made in this way with either the crown or the cylinder process (Chapter 10.8), production of flat glass was very labor-intensive, restricted to relatively small sheets and subject to wastage when cut into pieces for use. Besides, it did not yield high-quality products as is obvious to anyone looking at an old window where objects are often seen distorted through the glass in which defects and streaks are also generally present as a result of the detrimental effects of temperature or composition heterogeneities that could not be avoided during the melting and forming processes.

Mechanization was pioneered from 1894 to 1916 by J. H. Lubbers at the American Window Glass company. Glass cylinders of constant diameter and wall thickness began in 1904 to be blown successfully with a well-controlled low-pressure air flow issued for 15–18 minutes from a machine that was dubbed *iron lung* [1]. Making much bigger cylinders, which eventually reached 1 m in diameter and more than 13 m in length (Figure 1), did reduce considerably cost and labor (whence the very strong Union opposition met by the new process), but did not result in consistently good quality because of the wavy surface and optical distortion induced by the flattening stage. Thanks to *updraw* processes designed in Belgium and in the United States, it then became possible in the following decade to bypass the hollow-glass step. But these processes remained discontinuous because devitrified material had to be removed periodically from the production line.

A true revolution in glass producing thus occurred when the float process was introduced in the 1950s to produce sufficiently good flat glass to make the grinding and polishing steps ensuring high-quality sheets obsolete. Production became in addition completely continuous, which allowed the productivity to be considerably increased without affecting surface quality. Because of the very large amount of glass produced, however, the float process may be impractical when production volumes are small or the glass composition has to be changed frequently. For specialties such as crown glass for niche markets or new glass for electronics markets, older processes are thus still used or new ones have been designed to achieve in particular a high flexibility of throughput and broad ranges of thickness and width.

In this chapter, we will review the various processes that have been designed to achieve these goals, beginning with the first developed ones whose interest is now only historical. The early processes are denoted as *updraw* because

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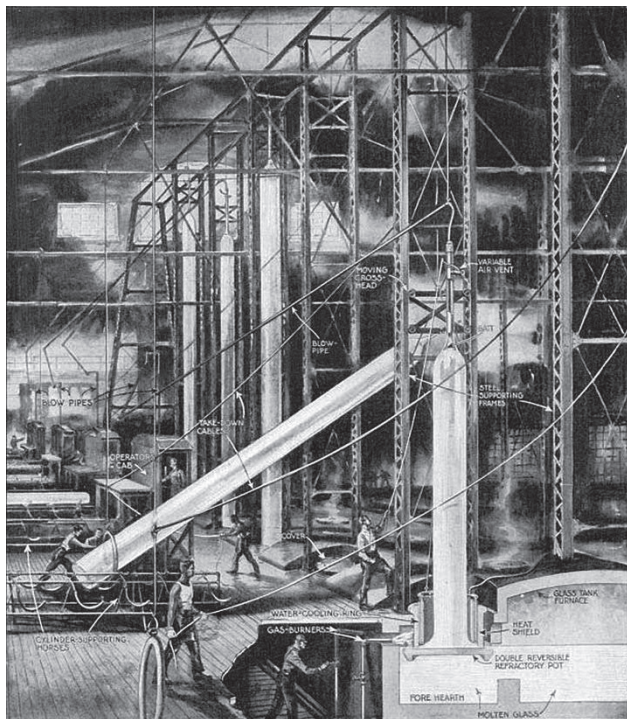


Figure 1 Very large glass cylinders blown mechanically with the Lubbers process for flat-glass production [2].

the glass was drawn upward, in contrast to the *downdraw* processes, which have subsequently been developed for specialty glasses. No attention at all will be paid to the synthesis of the glass itself, which is described in Chapter 1.3. The emphasis will thus be put on the forming process and on the material parameters such as viscosity, density, heat capacity, and surface tension that control it. For more detailed descriptions, the reader will be referred to the available technical literature [1–9].

2 Overview

The main features of past and current processes are summarized in Table 1. Although updraw processes are no longer used for commodity applications, it remains worthwhile to examine their mechanisms and forming principles from a technological viewpoint. For flat-glass forming, the essential requirement is to achieve the constant desired thickness, which now ranges from around 25 mm to less than 50 μm , with the specified width at a commercially admissible cost. Additionally, a flatter and smoother surface is requested. The essential forming defects are mainly of two kinds depending on whether they are derived from locally uneven deformation or undesirable stress. The former is caused by viscosity heterogeneity of glass originating from chemical impurities

or temperature irregularity, and the latter is caused by fluctuation of forming condition or stress imbalance.

Architectural glass must, for instance, satisfy appropriate transparency and reflection, but glass for automobiles and electronics products has to meet much more demanding quality specifications even for thinner glass whose production becomes increasingly difficult.

In all forming processes, two distinct steps are involved once the glass has been melted at about 1500 °C, refined, and homogenized in the melting tank. The first is its delivery under conditions at which the temperature, thickness, and flow rate must be as stable and uniform as possible throughout its whole width at a viscosity of about 10^2 – 10^3 Pa·s (i.e. at 1200–1000 °C for soda-lime silicate). In the second step, the more viscous molten glass cooled down to a temperature at which the viscosity is 10^3 – $10^{6.65}$ Pa·s (i.e. at 1050–700 °C for soda-lime silicate) is stretched in the longitudinal direction, while minimizing simultaneous narrowing of the glass ribbon.

In both glass delivering and stretching systems, properties of the molten glass such as surface tension, gravitational force, and tensile stresses are critical factors, whereas the kinetic aspects of the process are tightly controlled by means of drawing chambers, *débiteuses*, draw bars, rolls, float baths, slots, fusion pipes, etc. Besides, heat management through variously devised heaters and coolers is another fundamental aspect because glass properties vary very strongly with temperature. In addition to physical effects, one must also take into account chemical factors such as possible devitrification and chemical reactions between the glass and other materials, which may themselves depend on glass composition.

Since annealing follows forming, the conditions of the former process are greatly influenced by those of the latter. The formed glass ribbon is cooled down and conveyed to an annealing *lehr* where the decreasing glass temperature is carefully controlled so that residual stresses caused by viscoelasticity are relaxed between the annealing and strain points (10^{12} Pa·s, 570 °C, and $10^{13.6}$ Pa·s, 530 °C, respectively, in soda-lime silicate), and breakage caused by thermal stresses is minimized upon cooling down to room temperature. Finally, optical devices are installed at the downstream part of production line to detect in the glass at room temperature any visible defects such as bubbles, stones, streaks, etc., which originate either from the melting tank or the forming process. These defects are at once clearly marked on the glass ribbon and their positions are usually electronically recorded for optimized cutting either at the end of the production line or by the user according to its specific application. For flat glass to be used in buildings, any 10 m^2 -sheet must, for instance, have fewer than three defects with a maximum size of 1 mm (which would be tantamount to finding fewer than three coins on a football field!).

Table 1 Comparison of forming processes.

Category	Process	Mechanism		Advantage	Disadvantage	Current situation
		Step 1: Preliminary forming (Molten glass delivering)	Step 2: Main forming (Stretching)			
Updraw process	Fourcault process	Glass flow toward débiteuse and upward flow through débiteuse slot	Upward drawing against gravity by pairs of rolls	Earliest continuous production Smaller investment	Quality (Draw lines) Cyclic operation	Almost obsolete for commodity applications Customized/modified process operating for specialty glass
	Colburn process	Glass flow toward drawing point and upward flow from free surface	Upward drawing against gravity by pair of knurled rolls and bending roll	Higher output Wide range of thickness	Low surface quality Complex operation	
	Pittsburg Pennvernon process	Glass flow around draw bar and upward flow above draw bar	Upward drawing against gravity by pairs of rolls	Better surface quality Longer cycle	Distortion Thickness deviation	
	Asahi process	Glass flow toward Asahi blocks and upward flow through gap between Asahi blocks	Upward drawing against gravity by pairs of rolls	Smaller investment Longer cycle	Cyclic operation	
Roll out process	Continuous double roll process	Horizontal glass flow through forehearth	Pressing by pair of rolls	Value added with patterns and wires Versatility Smaller investment	Limited applications	Popular for patterned glass, wired glass, and specialty glass
Float process	For thinner sheet (Top roll process)	Viscous flow with equilibrium thickness in upstream area of bath	Horizontally stretching by conveyor rolls and top rolls	Large-scale production (productivity) Quality (flatness) Flexibility for thickness and width	Large investment Constraint of chemical elements in glass	Widely operating in the world for various applications
	For thicker sheet(Fender process)	Viscous flow with restricted width by pair of fenders	Cooling to appropriate temperature in fender area (without stretching)	+ Thicker and larger sheet		
Downdraw process	Slot downdraw process	Glass flow toward slot and downward flow through slot	Stretching by pairs of rolls and gravity with anchored to slot	Thinner glass Small-scale production	Flatness and surface quality Limited width	Customized/modified process operating for specialty glass
	Fusion downdraw process	Glass flow through trough and over weirs, downward flow on both sides of fusion pipe	Stretching by pairs of rolls and gravity with anchored to root	Thinner glass High surface quality	Minute control required (temperature, glass flow) Constraint of liquidus viscosity	Popular for specialty glass

3 Updraw Processes

3.1 Fourcault

The first manufacturing method successfully industrialized and commercialized was invented from 1901 in Belgium by É. Gobbe and É. Fourcault and finally implemented industrially in 1912 by É. Fourcault in his family company in Charleroi. With this process, the molten glass was drawn vertically through a débiteuse into a continuous glass ribbon. The débiteuse, a rectangular refractory piece with a spindle-shaped slot at the center, was immersed into the molten glass. The molten glass flowing up from the slot was drawn upward and immediately cooled by the coolers while conveyed upward by pairs of rolls in a such a manner that its width was kept constant. The formed glass was annealed along the way and finally cut off at the top of the 8–10 m drawing tower (Figure 2). The flow rate was controlled by the immersion depth of the débiteuse, the shape of the slot, and the cooling exerted, whereas the thickness of the sheet was determined by the drawing speed.

The advantages of this process were many. Not only could production be made with several drawing machines for a single glass tank, but wide ranges of thickness (1–8 mm) and width (1.5–2.5 m) were possible for glass sheets formed with a relatively uniform thickness. In terms of disadvantages, continuous operation was impossible because of the need after about two weeks of operation to remove the devitrified glass that was accumulating around the slot of the débiteuse and on the inner surfaces of the drawing kiln. Whereas the former devitrified

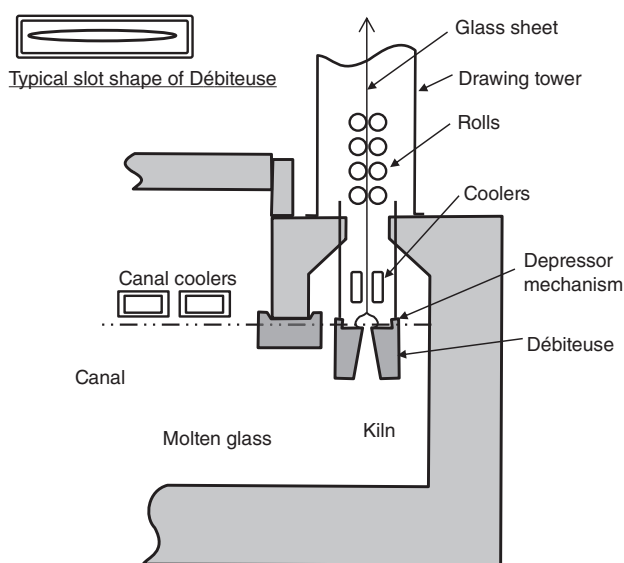


Figure 2 Sketch of Fourcault process in cross section. The molten glass flows up through the débiteuse slot and is drawn upward [3].

material was causing draw lines, the latter changed the flow rate and flow pattern toward the débiteuse. In addition, it was impossible to maintain a completely stable throughput because of bubble formation at the beginning of a drawing cycle and draw-line problems and instability toward the end [1, 3–6].

3.2 Colburn

At the same time the Fourcault process was being developed, the American inventor I. W. Colburn (1861–1917) was experimenting vertical drawing without a débiteuse. His first patent was taken in 1902 but the company he founded in 1906 to produce glass went bankrupt five years later. Working thereafter for the Toledo Glass Company, which had bought his patent, Colby was eventually successful in 1913. With his process, the molten glass introduced into a shallow drawing chamber was drawn upward from the free surface, its edges being gripped and driven by pairs of knurled rolls, and cooled immediately. After being reheated by a gas burner, the formed glass was brought horizontally by a bending roll and conveyed to a horizontal annealing lehr (Figure 3). Since the surface condition and flatness of the bending roll directly determined the quality of the glass sheet, the choice of an appropriate metal as well as the surface treatment and temperature control of the bending roll were crucial. Typically, two drawing chambers were mounted on one glass tank. The 0.9–6 mm thickness range obtained was similar to that of the Fourcault process, but devitrification on the débiteuse was avoided and a much larger width of up to 4.2 m could be obtained, thanks to the horizontally conveying process. But the price to be paid was a lower glass quality because of thickness variations, optical distortions, and surface defects [1, 3–6].

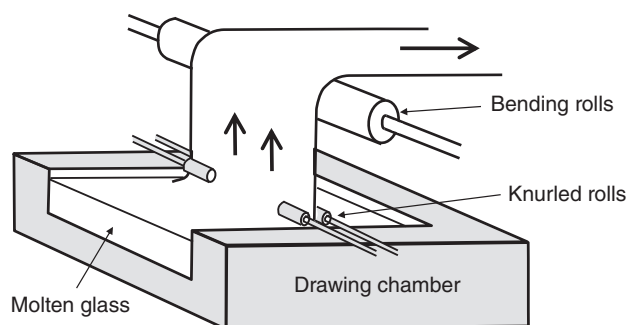


Figure 3 Sketch of Colburn process in a bird's-eye perspective. The molten glass is drawn upward from the free surface and bended horizontally by a bending roll [6].

3.3 Pittsburgh Pennvernon

A process similar to that of Fourcault was developed and introduced by the Pittsburgh Plate Glass Company in 1926. In this Pittsburgh Pennvernon process, the molten glass was not drawn through a *débiteuse* but upward from the free surface right above a drawbar, which was a long and thin refractory part immersed below the glass surface. The ribbon width was kept constant because the glass was cooled by edge folks and coolers. After being annealed and cooled in the drawing tower, the glass ribbon was cut off at the top of the tower (Figure 4). The drawbar served to anchor the drawing point and to ensure uniform temperature and glass flow rate across its width. In addition, ell blocks served to homogenize the drawing temperature by keeping the glass melt covered. The operation cycle was much longer than that of the Fourcault process with a better surface quality and without devitrification complications. Typically, the thickness range was 1–8 mm with a width of up to 3.2 m, but the disadvantages were thickness variations resulting from temperature fluctuations and inhomogeneities in chemical composition caused by drawing of the glass directly from its surface [3–6].

3.4 Asahi

The most recent updraw process has been developed by Asahi Glass Company around 1970 to overcome in a new way the disadvantages of the Fourcault process [5, 6, 8]. With it, a pair of hourglass-shaped rolls, called “Asahi blocks,” is immersed into the molten glass instead of a *débiteuse*

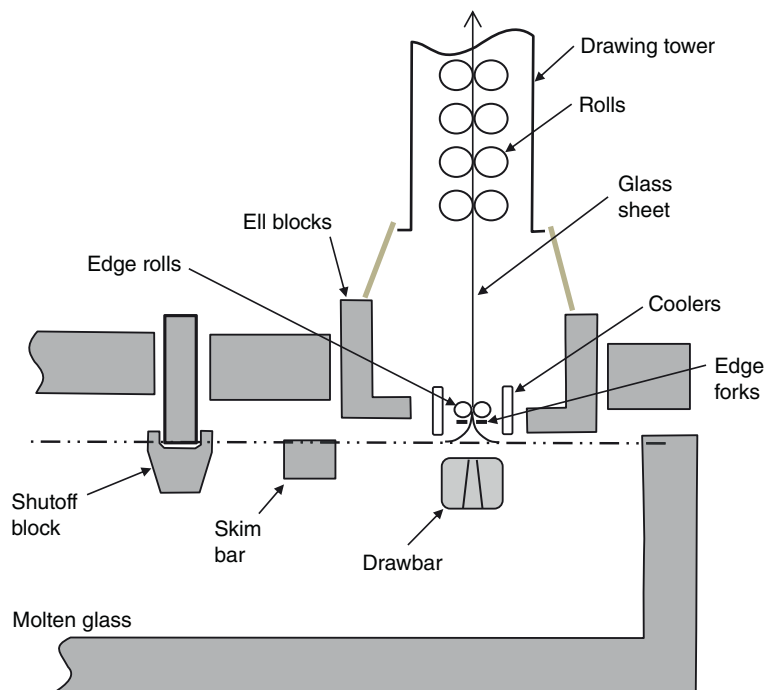
(Figure 5). The trick then is to make the Asahi blocks rotatable to renew the parting line where the glass leaves from the refractory and devitrification takes place. As a result, much longer drawing periods of up to 2–4 months can be achieved. An additional advantage is that thinner sheets down to 1.1–0.7 mm can be produced, especially for electronics applications, with a width of 1.5–2 m, thanks to the forming stability derived from the Asahi blocks.

4 Roll Out Process

The continuous double-roll process was developed in the United States in an effort led by the Ford Motor Company to meet a growing demand from the automotive industry. As delivered from the forehearth, the molten glass was pressed to a given thickness, cooled rapidly by a water-cooled pair of rotating rolls, and then conveyed into a horizontal annealing *lehr*. The thickness was determined mainly by the gap between the rolls, whereas the output was fixed by the rotating speed of the rolls.

As made by Pilkington Brothers in the 1920s, this process was then improved to manufacture plate glass through online grinding after annealing, followed by polishing of the cut plates. The process was further developed by Saint-Gobain in the 1950s to grind *and* polish on line the glass ribbon (Chapter 10.9). Along with a waste of about 20% of the glass, very high investment and operating costs were major disadvantages of these mechanical methods, however, which in fact prompted Pilkington to develop the float process as described in Section 5.

Figure 4 Sketch of the Pittsburgh Pennvernon process in cross section. The molten glass is drawn upward from the free surface right above the drawbar immersed below the glass surface [3].



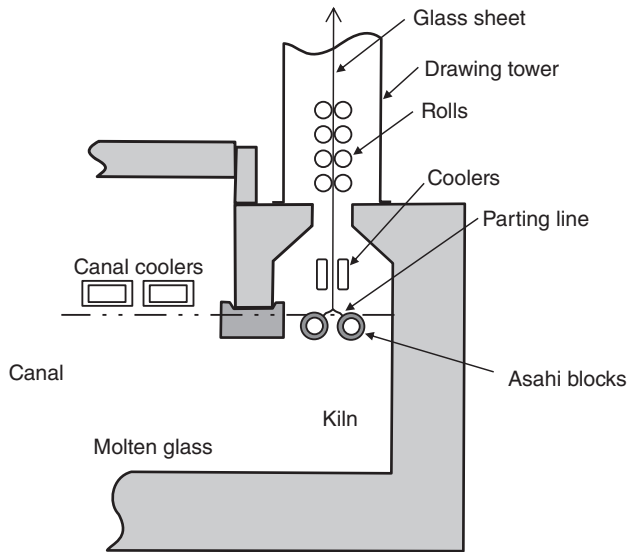


Figure 5 Sketch of the Asahi process in cross section. The rotatable Asahi blocks are immersed into molten glass instead of the *débiteuse*, and enable the parting line to be renewed where devitrification takes place [6].

Because the float process was not designed at all for patterned and wire-reinforced glass, the continuous roll out process, with which these products have been produced since the 1920s, has escaped oblivion (Chapter 10.9). Thanks to its versatility and facility for customization, it has even found new special applications, for instance, to make cover glasses for solar cells with excellent light diffusion through patterned textures on the surface. Usually the pattern is impressed on the lower surface by the lower roll, which is engraved. Generally the thickness range is 2–7 mm for the patterned and 8–25 mm for the polished glass.

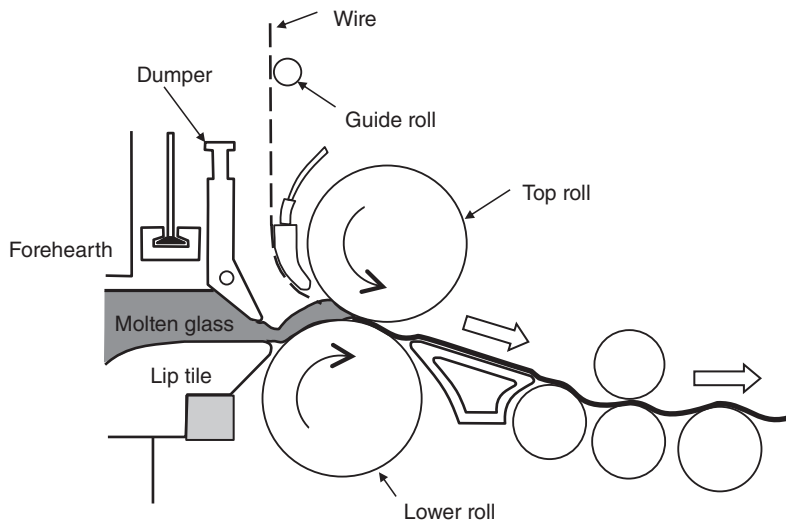


Figure 6 Sketch of single-pass wire roll out process (upper part insertion process). The wire is inserted into the molten glass, which is pressed and cooled by rotating water-cooled rolls [8].

As to wire-reinforced glass, it is produced in two ways depending on whether the wire is simply inserted into a molten glass (single-pass process, Figure 6) or sandwiched between two glass layers (double-pass process). Although more complex, the latter process has advantages over the former in terms of larger output, wider width, and higher quality, and better suitability for subsequent conversion into polished wired glass because the wire mesh is always precisely located at the center in the thickness direction [1, 3–8].

5 Float Process

5.1 Principle

When it was invented in the 1950s, the float process turned out to be an epoch-making method to produce flat glass with a smooth surface without any additional polishing. Its production cost was low enough to make possible an extensive use of the material in buildings and automobiles, which is one of the hallmarks of current civilization. The basic process of making flat glass on a molten metal was in fact patented in various ways as early as in 1848 in England by H. Bessemer, of steel-converter fame, and then several times in the United States by W. Heal and J. H. Forrest (1902 and then in 1925), and by Halbert K. Hitchcock (1905 and 1925), but a great many technical problems had to be solved before the process could be made practical. Through a seven-year expensive research program of Pilkington Brothers in the United Kingdom, which in its last stage included 13 months of production that had to be discarded, all these problems had eventually been overcome in July 1958 by a team led by L.A.B. Pilkington (no relationship with the Company's owners) and K. Bickerstaff. The following year it

even became possible to produce with the same process the distortion-free glasses needed for mirrors, thus abolishing the long-standing distinction between window and polished-plate glass (Chapter 10.9).

Although the float process became continuously profitable only in 1963, the previous year it began to be licensed all over the world by Pilkington Brothers in rapidly expanding markets. Within a decade, the good optical quality of float glass resulted in a vanishing share for other sheet- and plate-glass processes. As of 2015, more than 400 float plants are operated worldwide, units being up to about 500 m long (Figure 7). With a typical size of about 25×60 m, melting tanks are bigger than Olympic swimming pools to produce 600 metric tons (and even up to 1300 tons in the biggest plants) of flat glass per day with an investment cost ranging from 70 to 200 million dollars or euros, depending on actual size, location, and product complexity. As for the inflation-adjusted production cost (cf. Chapter 9.6), it has been almost continuously decreasing by a factor of 4 from 1965 to reach today a range of 200–300 dollars or euros per ton (Chapter 9.6), raw materials and energy accounting both for about 20% of it.

When a molten glass is poured onto a clean molten metal bath, it floats, thanks to its much lower density, spreads out, and thins to the point where the gravitational forces and the surface tensions among the glass, molten metal, and atmosphere are in equilibrium to reach the so-called equilibrium thickness. The lower and especially the upper surfaces of the molten glass are fire-polished, perfectly flat, and parallel except at the edges. The float process is based on this principle. Among metals or alloys

that are liquid between 600 and 1050 °C, the relevant temperature range for glass forming, pure tin was the obvious choice because of its low melting temperature of 232 °C, high density of about 6.5 g/cm^3 at 1000 °C, low vapor pressure of about 10^{-7} atm at 1000 °C, high boiling point of 2602 °C, low reactivity with silicates in the metallic state, and not too high cost (about 20 dollars/kg as of 2015).

The aforementioned equilibrium thickness T_e is given by

$$T_e^2 = 2\rho_t(S_{ga} + S_{gt} - S_{ta}) / [g\rho_g(\rho_t - \rho_g)], \quad (1)$$

where S_{ga} , S_{gt} , and S_{ta} are the surface tensions at the glass–atmosphere, glass–molten tin, and tin–atmosphere interfaces, respectively, g is the gravitational constant and ρ_t and ρ_g are the density of the molten tin and glass, respectively (Table 2). For soda-lime silicate glass floating on clean molten tin under a nitrogen-hydrogen atmosphere, T_e is 6.9 mm (Figure 8), a thickness that is actually insensitive to small changes in the chemical compositions of the atmosphere, metal bath, or glass [1, 3–9].

5.2 Float Bath

The float bath contains several metric tons of molten glass. It is a large unit with a length of up to more than 50 m enclosed by a steel shell that is lined with thick insulating and nonreactive refractory materials and holds a pool of molten tin whose depth is 50–100 mm and total amount is up to more than 200 metric tons kept at temperatures decreasing from about 1000 to 600 °C from the

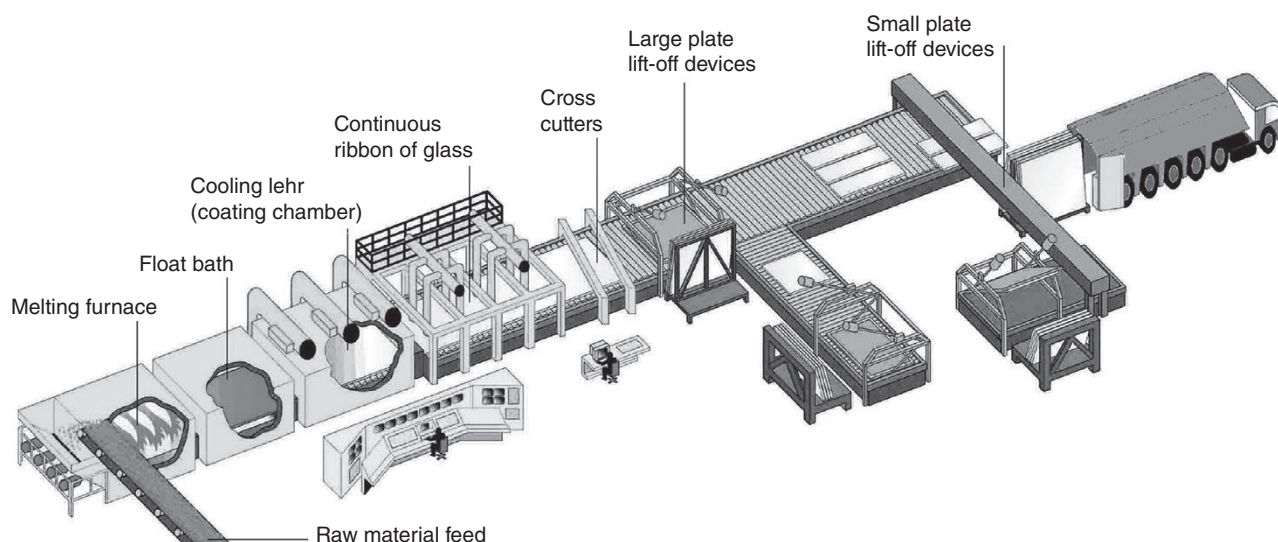
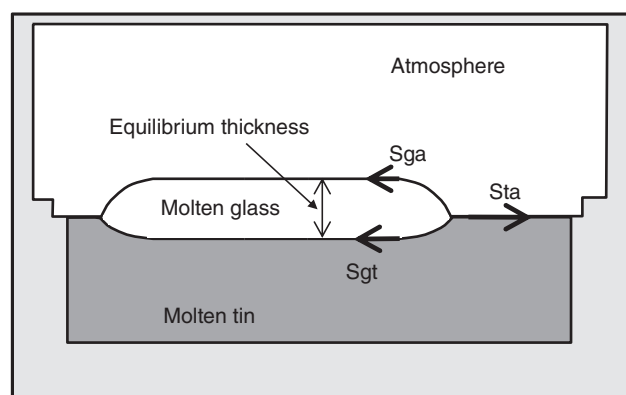


Figure 7 Overview of a float-glass plant (scale not right: size of the right-hand side, for instance, much exaggerated) <http://www.glassforeurope.com/en/industry/float-process.php>

Table 2 List of symbols regarding equilibrium thickness mechanism.

Symbol	Denotation
T_e	Equilibrium thickness
ρ_t	Density of molten tin
ρ_g	Density of molten glass
S_{ga}	Surface tension at glass–atmosphere interface
S_{gt}	Surface tension at glass–molten tin interface
S_{ta}	Surface tension at tin–atmosphere interface
g	Gravitational constant

**Figure 8** Equilibrium thickness of floating glass on the molten tin when the gravitational forces and surface tensions are balanced [3].

hot to the cold end (Figure 9). A reducing gas mixture made up of 2–8% hydrogen and 98–92% nitrogen is supplied at a high rate of the order of $10^3 \text{ m}^3/\text{h}$ from above to the bath to prevent oxidation of the molten tin and to maintain a positive pressure difference with the atmosphere at the bath exit where leakages are highest. The heaters, coolers, and other devices are installed and inserted in the bath. The molten glass is continuously supplied from the furnace conditioner via a canal where its flow rate is precisely controlled by an adjustable gate called a tweeel. It arrives to a ceramic spout lip, which is an inlet of the float bath, through which it falls freely onto the molten tin. After many years of struggle at Pilkington Brothers to achieve excellent quality, the design and engineering of the inlet area were an outstanding invention to force the contaminated molten glass in contact with the refractory lip to flow outwardly so as to be brought forward at the outer edges of the ribbon [9].

Once poured onto the tin bath with a thickness of about 50 mm, the glass spreads out and thins to its equilibrium thickness in the upstream area in the float bath. As formed to the required thickness and width in the forming area (see Section 5.3), the glass ribbon is taken

out from the bath either to receive appropriate reflective, low-emissivity, solar-control, self-cleaning, or other specific coatings (Chapters 6.7 and 6.8) or to enter directly the annealing lehr at the temperature at which the viscosity is about $10^{10} \text{ Pa}\cdot\text{s}$ (i.e. about 600°C for soda-lime silicate). At the end of the lehr, whose length can reach 120 m, the ribbon is finally cooled down to room temperature and brought into the cutting area. Whereas both edges are cut out (to be recycled as cullet) because of the imprint left by the top rolls, the ribbon itself is cut either according to customers' specifications or as standard sheets, for instance, $6.0 \times 3.21 \text{ m}$ in Europe where tools used in the flat-glass transportation industry have been fitted to this size (which, by the way, is too large to allow flat glass to be shipped in containers).

5.3 Thinner (Top-Roll Process) and Thicker (Fender Process) Glass Ribbons

For forming thin sheets, the molten glass with its initial equilibrium thickness in the upstream area in the bath is subjected at the same time to longitudinal and lateral forces. The former are exerted by conveyor rolls that stretch the ribbon from the annealing lehr and pull it at a typical speed of up to 25 m per minute. The latter are exerted outwardly on the ribbon edges by pairs of top rolls, which are water-cooled rotating gears, to reduce the narrowing of the glass ribbon because the imposed longitudinal stretching reduces not only its thickness but also its width (Figure 10a). In parallel, the glass ribbon is cooled down to prevent it from returning to its equilibrium thickness until its width is constant at the end of the forming area. In view of the fundamental influence of viscosity within the glass ribbon upon stretching and thinning, the temperature distribution and the top-roll operations must be controlled very tightly to ensure a good forming quality. Besides, keeping the glass ribbon as wide as possible is important to maximize productivity.

For producing float glass thicker than the equilibrium thickness, a pair of water-cooled carbon fenders serves as slipping guides to the flowing glass in the bath (Figure 10b). The glass thus proceeds with a restricted width and a large thickness. As it passes down the fender area, the effects of gravitational forces and surface tensions make both its upper and lower surfaces flat and thickness uniform. The glass is then cooled to an appropriate temperature in the downstream area of the fender where its viscosity is high enough not to allow width changes. In contrast to what is taking place in the top-roll process, stretching is not significant at all and there is no drive to return to the equilibrium thickness because there is no glass–tin–atmosphere interface in the fender area.

Figure 9 Sketch of the tin bath part of the float process: (a) on vertical plane along centerline; (b) on horizontal plane. A reducing nitrogen–hydrogen gas mixture is supplied from above. Heaters and coolers are installed [10].

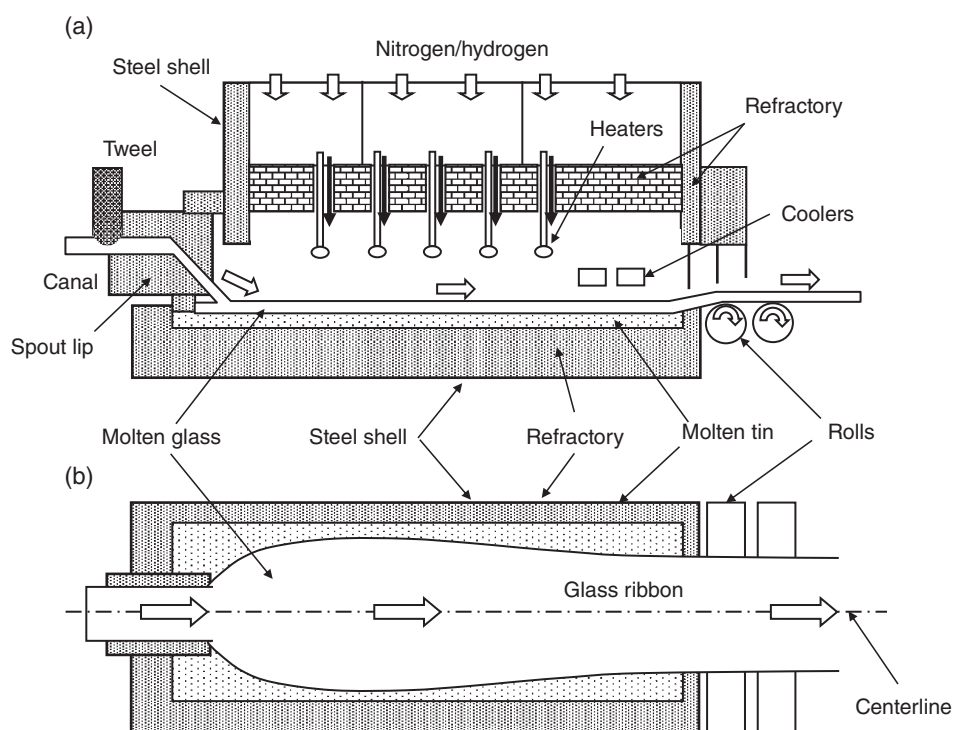
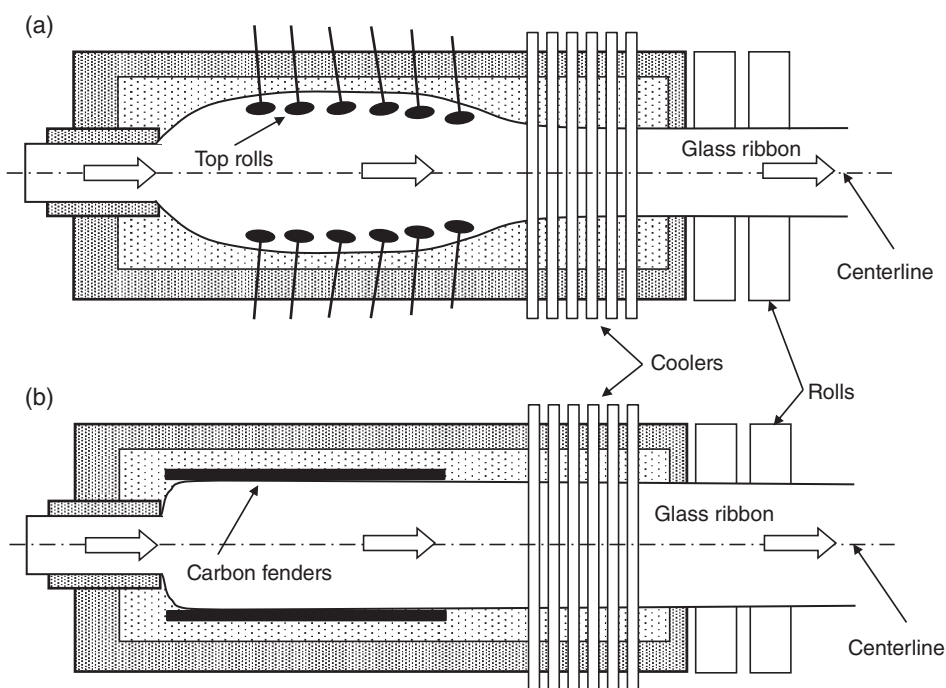


Figure 10 Sketch of the float process: (a) for sheets thinner than the equilibrium thickness, where the glass is stretched, from its edges by top rolls and from its downstream part by conveyor rolls; (b) for sheets thicker than the equilibrium thickness, where water-cooled carbon fenders serve as slipping guides to glass flowing [7].



5.4 A Complex Industrial Problem

In spite of the simplicity of its principles, the float process is not readily implemented because flow in both tin and glass and heat transfer among tin, glass, and the radiative field are really complex processes. Glass

forming is mainly determined by parameters such as the glass flow rate, conveyor speed, rotating speed and angle of top rolls, and by the viscosity distribution within the glass ribbon. It goes without saying that the viscosity of the glass strongly depends on temperature, but the temperature distribution in the bath is itself influenced

by radiative heat transfer, the flow of molten tin, and the glass forming conditions. Radiative heat transfer is predominant in the bath at temperatures higher than 600°C , but the flowing molten tin also contributes markedly to heat transfer as a result of its high heat capacity, high thermal conductivity (about 50 times higher than that of the glass), and low kinematic viscosity (about 8 times lower than that of water), whereas the glass flow carries a large amount of convective heat. On the other hand, molten tin flows by traction from the glass ribbon (i.e. velocity distribution) and buoyancy convection (i.e. temperature distribution in the bath). In order to understand forming conditions, one thus needs to understand the whole set of processes taking place in the bath since glass forming, heat transfer in the bath, and flow of molten tin affect one another in a very complex manner.

As summarized by C.K. Edge [4], the float bath thus is “a remarkable entity which, although first envisioned as a finisher of glass surfaces, also functions as a container, a conveyor, a forming unit, a chemical reactor and a heat exchanger.” In view of this complexity, valuable information has been drawn from mathematical simulations not only of the glass forming mechanisms, but also of the temperature field and the mutually related dynamics of the molten tin and glass ribbon. As examples, calculations with finite-element methods of the thickness contour over the glass ribbon and of the lateral thickness distribution of the ribbon at the bath exit are shown in Figures 11 and 12 [10]. The rather good agreement of such model values with the temperatures, thicknesses, or ribbon shapes that can be measured on line illustrates how simulations can be used to optimize the operating conditions, to design new facilities, and to check new ideas for process improvement and development.

From a chemical standpoint, potentially annoying impurities are oxygen from leaks or the $\text{N}_2\text{--H}_2$ gas mix, and sulfur originating from the molten glass. Both deteriorate productivity and glass quality if they induce alteration on the bottom surface of the glass caused by reactions with tin, and contamination adhesion on top and bottom surfaces (Chapter 5.6). In the so-called oxygen and sulfur cycles (Figure 13), SnO and SnS vapors form, condense, and precipitate, the former as SnO_2 and the latter as SnS (which is ultimately reduced to Sn particles). Thanks to extensive research, however, these impurities are now carefully managed through monitoring, sealing, cleaning, atmosphere controlling on flow and pressure, etc.

5.5 Trends in Float Production

The float process is advantageous because it yields excellent flatness, high flexibility with regard to thickness and

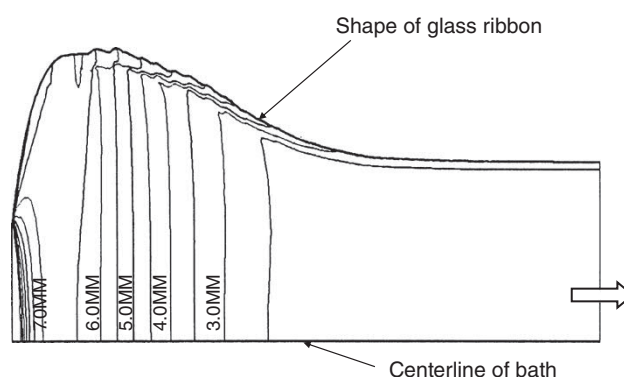


Figure 11 Shape and thickness distribution of a 2 mm thick float-glass ribbon calculated with an integrated glass-forming model [10]. Forming (i.e. shape, thickness, and velocity distributions of the glass ribbon) and the flow of molten tin are first calculated for a given temperature distribution of the glass ribbon. Heat transfer (i.e. the temperature distribution) in the float bath then is simulated, and the whole calculation is iteratively repeated until convergence is reached for the three interrelated mechanisms.

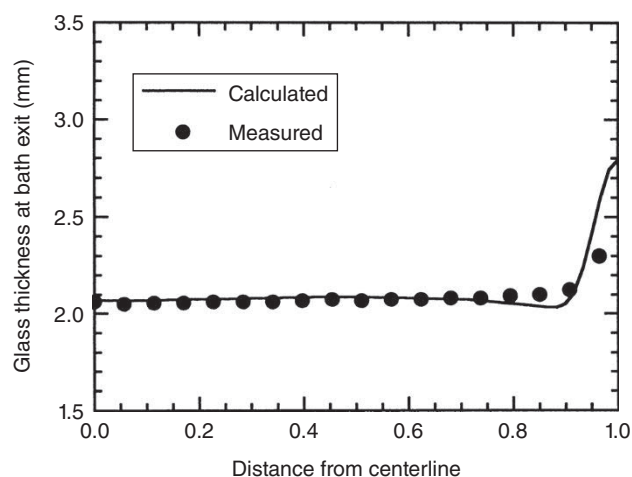


Figure 12 Simulated thickness distribution at the exit of the bath for 2 mm thick glass ribbon. The lateral distance is normalized [10].

width, and high productivity owing to completely continuous operation during the whole lifetime of the melting furnace, which can now reach up to two decades. Ever since its conception, plenty of technological improvements have been conducted for achieving higher throughput, larger width, and higher still quality, the thickness currently extending down to less than 0.4 mm and up to around 25 mm.

Originally the float process was designed to produce glass sheets for architectural window and mirrors. Since the 1970s, the technology has evolved to meet other demands, especially that emerging from automotive

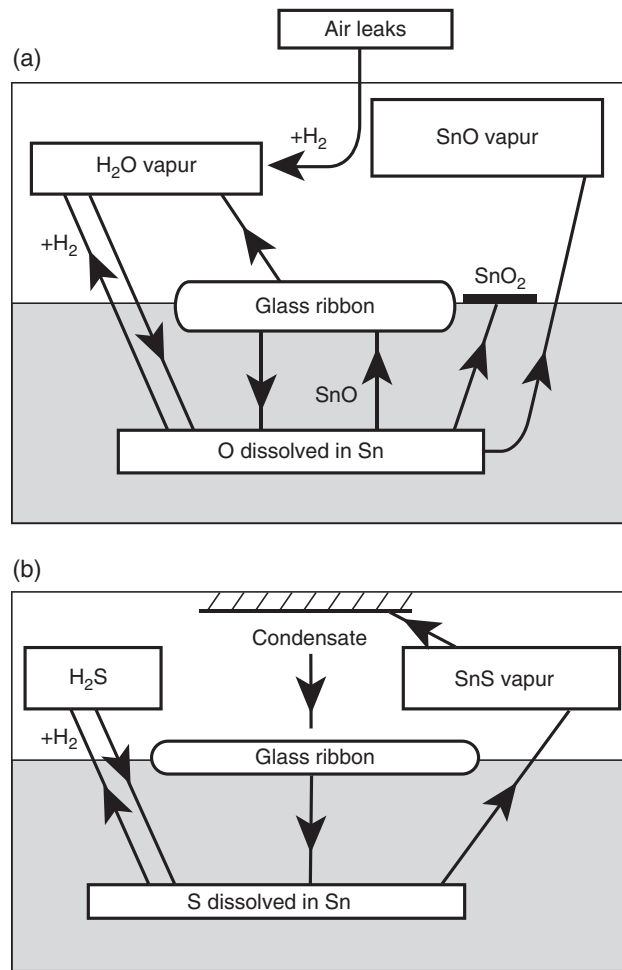


Figure 13 The complex interactions of impurities with the atmosphere, tin bath, and glass ribbon in the float process: (a) oxygen cycle; (b) sulfur cycle. Source: After Pilkington [9].

market for higher optical quality and thinner sheets along with higher throughput to keep production costs reasonable. In addition, the float process has contributed to the growing solar generation market with products such as mirrors for solar power systems and cover glasses for photovoltaics.

In the early 1980s, the float process achieved production of ultrathin glass of less than 1.1 mm for twisted nematic (TN)/super TN (STN) liquid crystal display (LCD) substrates, touch panels, and other electronics products with a remarkably high quality for flatness, thickness constancy, defect level, etc. Beginning in the 1990s, the float process has been producing flat glass of various kinds of compositions other than the traditional soda-lime silicate. Examples are alkali-free glass for thin film transistor (TFT) LCD substrate, high strain-point glass for plasma display panel (PDP) and solar panel substrates, specialty glasses for heat-resistant products, hard

disk drive (HDD) substrates, and other products such as touch panels and display covers that are then chemically strengthened.

6 Downdraw Processes

6.1 Slot Downdraw

It was for forming thin glass sheets that the slot down-draw process was developed in the 1940s. As driven by pairs of rolls, the molten glass is pulled downward through an accurately dimensioned narrow slot, made of platinum, which is fixed at the bottom of the fore-hearth. The glass sheet pulled from the slot is then gripped on its edges to prevent narrowing (Figure 14). The suitability of this process for making thin glass stems from the fact that a viscous molten glass can be pulled downward with a higher speed than if it were just subjected to free fall [3, 7, 11].

6.2 Fusion Downdraw

The slot downdraw process has disadvantages in terms of imperfect flatness and other defects caused by slot deformation and foreign contamination on the inside of the slot. It was to overcome them that the fusion downdraw process was developed by Corning [3, 5, 7, 11]. As sketched in Figure 15, the well-stirred molten glass is delivered through a conduit tube to one end of a rectangular trough that is the upper part of a fusion pipe. The molten glass flows over the weirs uniformly along the full length of the trough and then runs down on both sides of the fusion pipe. Two glass streams join and merge together at the "root," which is a bottom apex of the fusion pipe. A pair of rolls grips the edges of the glass sheet just below the root to prevent the sheet from becoming narrower as it is stretched downward. The glass sheet is then cooled down while its edges are still held by pulling rolls as it proceeds through a vertical annealing lehr, and is finally conveyed to the cutoff station. The distinguishing advantage of the fusion downdraw process thus is that the glass is formed without touching anything except air so that one obtains a smooth and defect-free fire-polished surface. To be achieved, however, this result requires a highly homogeneous molten glass and a minute control of the distribution of glass temperature and flow.

Since the 1960s, the fusion downdraw process has produced photochromic glass, heat-resistant glass, and glass for chemically strengthening. It provides ultrathin specialty glass of less than 1.1 mm thickness used for electrical capacitors, microscope slides, optical filters, touch panels, micro electronic mechanical systems (MEMS),

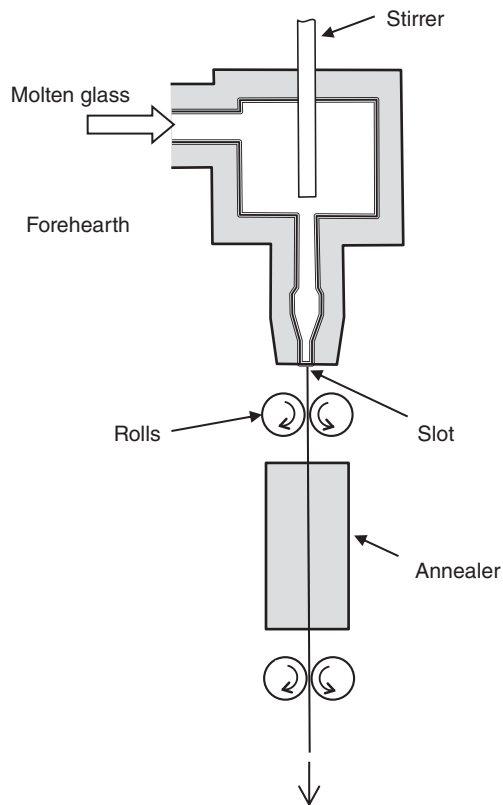


Figure 14 Sketch of slot downdraw process in cross section. The molten glass is pulled downward through a narrow slot driven by rolls [7].

substrates of TN LCD, and thin film solar cells. Besides, production of alkali-free glass for TFT LCD substrate was started in 1984 by Corning. Although the specifications are in this case much more severe, the fusion glass can also be used for TFT LCD substrate without polishing,

thanks to its excellent surface quality. To meet the market demand for larger size substrates, the width has been extended up to around 3 m. In addition, the downdraw process is applied to specialty glass for emerging chemically strengthened products such as touch panels and display covers.

7 Perspectives

Over the years the demand for flat glass has paralleled the growth of the global economy. In addition to architectural applications, the automotive, solar energy, and electronics especially flat panel display (FPD) application markets have all been at the same time growing and an important source of new, value-added products (Chapter 6.10). Recently, glass sheets for chemically strengthened components such as cover glass for displays and ultrathin glass for touch panels have emerged as important products driven by the explosive diffusion of mobile phones and tablets with touch sensors [12]. These trends are supposed to continue and affect markets such as appliance, transportation, interior architecture, and many others. The important role of flat glass keeps increasing in these domains as well as in the field of information and communication, optics, healthcare, and so forth. Further improvements will thus be made to meet new specifications and respond to various market demands. From an industrial perspective, however, not only the cost and quality of the glass itself but also controllability, investment size, yield, delivery time, versatility, cost of post-processing, and other factors of the manufacturing process have to be taken into consideration for each application. Therefore, an overall and comprehensive understanding of the forming process remains a key issue.

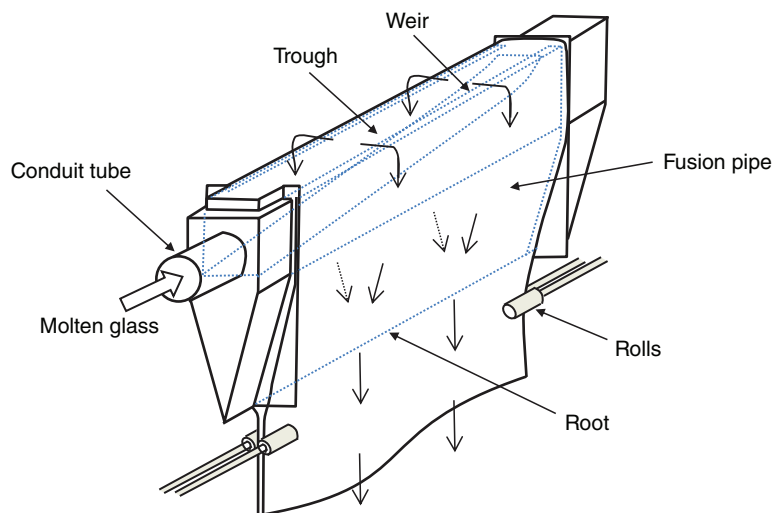


Figure 15 Sketch of fusion downdraw process in a bird's-eye perspective. Molten glass flows over weirs and run down on both sides of fusion pipe. Two glass streams join and merge together at the root and are stretched downward [3].

For new applications, work is in particular being conducted on ultrathin flexible glass (0.2 mm–30 μm) and on rolled glass for flexible display, OLED lighting, and organic thin-film solar cell to take advantage of unique features of glass such as bendability, impermeability to gas, transparency, surface quality, chemical and thermal durability, and so on [13]. Such products are not yet on the mass market because the fundamental technologies are not mature, but flexible and rolled glasses are nonetheless expected to come out in the near future. The applications to the field of health care, electrical and optical packaging, MEMS, and so forth are anticipated to become more popular as well [14]. The relevant information can be found on the websites of glass manufacturers.

Two directions for development of the forming process can be followed. One is to improve further currently existing processes in terms of flatness, thickness, width, productivity, controllability, cost, versatility, facility life-time, etc. The other direction is to add values through online introduction of other features such as coating and surface treatment (cf. Chapters 6.7 and 6.8). A closer match and harmonization between forming process and glass composition and properties might be also attractive.

As for forming commodity glass, invention of a novel process surpassing float with regard to energy consumption and investment costs would be desirable. For specialty glasses, innovative processes with higher quality and lower cost will of course also be sought after. Advances in basic science, simulation methods, sensing procedures, and information technology are presumed to become still more important either in operation and engineering or in development and innovation. Moreover, newly developed materials could make other innovative progress possible. In this respect, could unprecedented innovations based on novel mechanism make the processes described in this chapter obsolete in a near future? Their advantages should be considerable to write off the capital invested in current production plants all over the world. But would those innovations give rise to new applications and create new markets? A never ending challenge will change the world [15, 16].

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1.5

Fabrication of Glass Containers

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1 Introduction

At the beginning of the twentieth century, glass-container manufacturing still was a strenuous business, involving much manual labor and sweat. In 1903, Michael J. Owens developed in Ohio the world's first fully automatic glass-forming machine (Chapter 10.9). The concept consisted of a rotating machine that sucked glass from a pool of melt into forming molds. A preform of the final container (the so-called “parison”) was first produced, and then transferred into a second mold where the parison was blown to its final shape to form the container itself. This truly revolutionary concept gave major advantages over semiautomatic methods since it cut labor costs by 80% and also led to the end of child labor in glass-manufacturing companies. But this concept still had its drawbacks because the machine itself was expensive and cumbersome and a true monster of tons of rotated, lowered, and lifted metal.

In 1915, Karl E. Peiler and F. Goodwin Smith established a fully automatic press-and-blow rotary machine, which was fed with glass from above by an automatic paddle-needle gob-feeder (Chapter 10.9). Although this design resulted in a much less complex forming cycle, the machine was still a rotating system that involved again much mechanics and moving metal. And, most importantly, as soon as one section of a rotating machine experienced any problem, the machine as a whole had to be stopped. Hence, yield was significantly decreased when the complete machine had to be paused because only one section was experiencing problems.

With gob-feeding getting more and more sophisticated, a search began for a more efficient forming process. In 1924, F. Goodwin Smith and Henry W. Ingle developed a totally new concept for automated glass-container forming: the IS-machine, where “IS” stands for *Individual Section*. The machine sections were no longer arranged in a circle but in a row. This meant that each section of the forming machine operated independently from the others. Hence, if failure occurred in one section, just this section and not the complete machine had to be stopped and fixed. This made production much more efficient and flexible. Production speed and container quality also were greatly increased.

With 4 individual sections in the first IS-machine, the concept was soon improved and enhanced from initially 4 single gob sections (in total, therefore, 4 containers in one complete machine cycle) to nowadays 12 section-systems with multi-gob delivery to each section. In the most recent form, IS-machines can consist of 12 sections, with 4 forming molds per section (quad-gob system), summing up to 48 containers produced in one machine cycle.

Looking at a modern IS-machine, however, one should nonetheless recognize the basic features that were designed when the concept was first developed. As shown in Figure 1, one section is made of the following zones, which will be explained more in detail later in this chapter:

- 1) Delivery equipment, consisting of scoop, trough, and deflector.
- 2) Blank-side with plunger, neck-ring, guide-ring, mold-halves, and baffle.
- 3) Invert with invert-arm holding neck-ring and guide-ring.
- 4) Blow-side with bottom-plate, blow-head, and mold-halves.
- 5) Take-out with tongs, dead-plate, and pusher to conveyor belt.

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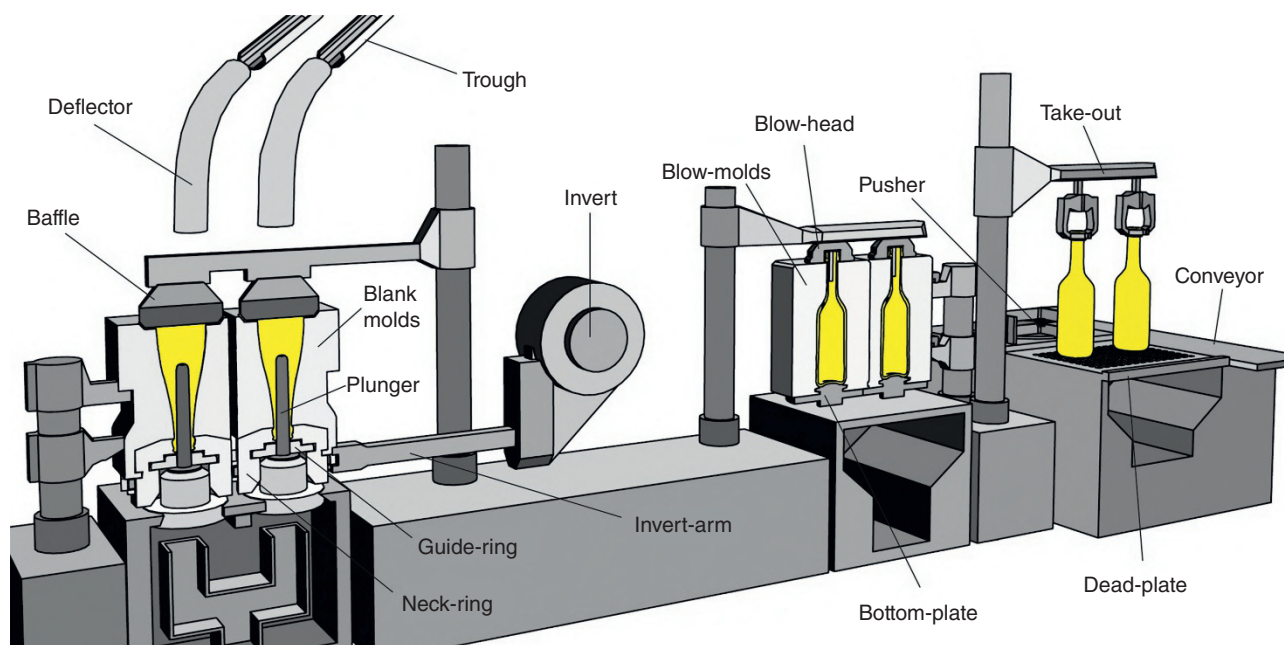


Figure 1 Schematic overview of one section of an Individual-section machine (here Narrow-Neck Press & Blow process, double-gob set-up).

Several major improvements have been implemented in the forming process since its beginnings. We will, for instance, describe how, following the *Press & blow* (PB) and *Blow & blow* (BB) processes, the *Narrow-neck press & blow* (NNPB) process has recently met with much success because of its more efficient forming. And it should also be stressed that the original pneumatic control of IS-machines has given way to servo-electric devices with which higher precision and reliability has been achieved.

2 Principles of Glass-Container Forming

Before a glass can be formed, it usually has to be melted out of the respective raw materials. The melting of container glass bears some peculiarities such as a high usage of foreign (external) recycled cullet or auxiliary devices such as batch and cullet preheaters. Because these features and the basics of the melting of container glass are described elsewhere in Chapter 1.3, we will focus solely on forming.

Glass containers for mass-market are formed with the aid of molds in which the molten glass is blown or pressed. The forming process consists of two steps. First a “parison” is made in cast-iron “blank-molds.” Then, in the second step, this parison is formed into the final container in “blow-molds” that are made of either cast iron or aluminum bronze.

2.1 Heat Management in Glass-Container Forming

A basic feature of the forming process is that it is highly non-isothermal. On the one hand, temperature differences over the dimensions of the glass component are present and on the other, the glass experiences a great change in temperature and thus in glass properties. As a result, the forming process has of course to be designed to cope with these changes, which are the largest for viscosity.

When the gob enters the mold in the first forming step, it has a bulk temperature of about 1050°C . The mold itself has a temperature of $450\text{--}520^{\circ}\text{C}$ at the end of the parison forming cycle, depending on forming conditions and container type. The glass–metal interface temperature T_C , which is a very important parameter for the forming, is almost constant (Figure 2) because of the short contact time t of only a few seconds between the gob and mold material. It depends on the temperature of the glass T_1 , on that of the contact material (mold) T_2 , and on the thermal conductivity λ , heat capacity C_p , and density ρ of both the glass and the mold material [1–3].

For soda-lime-silica glass, at the relevant temperatures these values can be taken as $\lambda \approx 10 \text{ W/m}\cdot\text{K}$, $C_p \approx 870 \text{ J/kg}\cdot\text{K}$, and $\rho \approx 2500 \text{ kg/m}^3$. For laminar cast iron, appropriate parameters are $\lambda \approx 55 \text{ W/m}\cdot\text{K}$, $C_p \approx 500 \text{ J/kg}\cdot\text{K}$, and $\rho \approx 7300 \text{ kg/m}^3$. From these values, one can estimate T_C with:

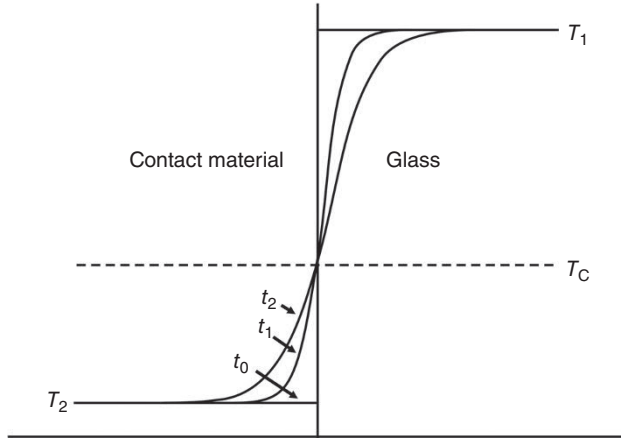


Figure 2 Temperature gradients and interface temperature between contact-material and glass over time.

$$\frac{T_1 - T_C}{T_C - T_2} = \frac{\sqrt{(\lambda \cdot c_p \cdot \rho)_{\text{mold}}}}{\sqrt{(\lambda \cdot c_p \cdot \rho)_{\text{glass}}}} \quad (1)$$

One finds in this way that temperatures of 1050°C for the gob and 470°C for the blank mold yield an interface temperature of ca. 614°C if no oxide layer resulting from corrosion of the mold is present and if the heat balance of the blank mold is correctly managed.

A certain cooling of the glass during the forming process is mandatory to achieve a stable enough product that does not lose shape in subsequent processes (handling, coating, etc.). If cooling is not applied correctly, too low a viscosity will prevent the parison from maintaining its shape and, thus, correct dimensions from being achieved and the final container from conforming to its specifications. In glass-container forming, this stabilization is realized, thanks to the surface layer of the parison that cools down through contact with the mold. Heat transfer thus is, in general, an important aspect in the forming of container glass. Not only large amounts of heat need to be removed from the glass, but heat transfer must be controlled locally to avoid internal tension that would build up if the shrinking rate were variable throughout the glass. The average heat transfer Q_{0-t} during the short contact period t between the glass and mold can be calculated according to

$$Q_{0-t} = \frac{\lambda_g \cdot \lambda_m}{\lambda_g \sqrt{\lambda_m / (c_p \cdot \rho)_m} + \lambda_m \sqrt{\lambda_g / (c_p \cdot \rho)_g}} \cdot \frac{2(T_1 - T_2)}{\sqrt{\pi \cdot t}} \quad (2)$$

where m designates the mold and g denotes glass properties. With the aforementioned parameters, one, for instance, finds a very large average heat transfer of 647 kW/m² for a typical forming cycle for which $t = 6$ seconds.

2.2 Interface Interactions in Glass-Container Forming

Whenever a glass container is formed through contact with a solid material, such as a mold or roller, the interface between the two bodies is a crucial point. From the preceding presentation, it appears that problematic situations occur when the interface temperature is either too high or too low.

If cooling of the mold is not rapid enough in relation to the gob temperature, the interface temperature between the gob and mold increases and at a certain point the glass begins to stick to the mold. The sticking temperature has a lower bound at which the glass still can be separated from the mold without significant damage. Nevertheless, reaching this lower bound leads to process failure because sticking of the glass causes a bad loading and an inhomogeneous temperature distribution, which themselves give rise to defects in the final container. At the upper sticking temperature, removing the glass from the contact material inevitably leads to damages of the glass, like checks or torn-out pieces.

The glass sticking temperature is widely independent of the type of the contact material. It is basically a function of the interface temperature T_C , but surface conditioning of the contact material may play a role as well. Sticking appears when the viscosity of the glass at the interface becomes lower than 10^{8.8} Pa·s [4, 5]. For an average container-glass composition that means sticking begins to take place when the interface temperature T_C between the gob and mold becomes higher than ~ 645°C.

The interface temperature of about 614°C calculated above is lower than the sticking temperature. However, it can easily happen in production that this temperature increases locally such that sticking of the glass does occur. This may happen because of changed cooling conditions, cooling failure, or the growth of an oxide layer on the molds, which significantly decreases thermal conductivity.

The friction coefficient μ between the glass and contact material plays a crucial role during forming. A low dynamic friction between the contact material and the glass favors a good gob-loading and glass-forming. Often the molds and the finish equipment are coated with a lubricant that decreases the friction. This so-called swabbing process is widely used in glass-container manufacturing. The swabbing lubricant mainly consists of graphite with various additives. Periodically, the molds are swabbed automatically by robot or by human hand to allow precise and stable forming. The swabbing intervals depend on the respective machine setup and container produced and can range between 15 minutes and several hours. The effect of swabbing on the friction coefficient is a temporary decrease in friction as well as a change in the heat-transfer characteristics between the glass and mold.

There are also different permanent and nonpermanent coatings available that can be applied to the mold and forming equipment to extend or even avoid the swabbing. Important physical aspects of gob-loading, including models of the mechanics of gob/blank-mold interaction and of dynamical friction, have been extensively discussed in papers to which we refer for further details [e.g. 6, 7].

2.3 Deformation Rates in Glass-Container Forming

As already pointed out, in container-glass manufacturing, the gob is first formed into the parison, and then the parison into the final container. The (de-)formation of both the gob and parison depends on the actual viscosity of the glass. A low forming- or interface-temperature leads to a high viscosity at the glass surface. Hence the glass surface starts to get “brittle.” If such a glass is then subjected to high deformation rates, as it happens not only upon pressing and blowing but also earlier in the process upon gob-cutting, it can experience too high tensile or shear stresses. The critical tensile stress σ_c (in MPa) that a hot soda-lime-silica glass can sustain at a given temperature T may be estimated from an empirically derived correlation [8]:

$$\sigma_c = \frac{4.8 \cdot 10^3}{\sqrt{T}} \quad (3)$$

Hot fracture occurs if the tensile stresses exceed this critical value. The maximum velocity $v_{\max}$ at which a glass container with a thickness d can be formed at viscosity η without experiencing hot fracture can be approximated by:

$$v_{\max} = \frac{\sigma_c \cdot d}{4\eta} \quad (4)$$

One thus concludes that at temperatures of about 1000°C, deformation velocities of ca. 500 m/s are, for instance, possible without hot fracture for a 2 cm-thick soda-lime-silica glass layer. At 900°C, the maximum allowed velocity is already down to 100 m/s and is lower than 10 m/s at 800°C. Below 700°C the risk of defects caused by hot fracture becomes significant. Because usually such defects cannot be inverted (“healed”) in later forming steps, care must be taken to prevent them from appearing.

3 Glass-Container Forming Processes

3.1 Glass Composition

For cost reasons, glass containers are made out of soda-lime-silica glass whenever special constraints do not

apply. An exception is, for instance, laboratory ware for which borosilicate glass is used instead (Chapter 7.7). Even though the forming process needs to be adapted to account for the specific properties of each glass type, the principles at work are similar for given kinds of containers. Three different forming processes are applied, namely BB, PB, and NNPB. Their main differences concern blank-side forming where the parison is made, the subsequent forming steps to make the final container being identical. As a matter of fact, many containers can be produced with more than one process so that there is much overlap between them in terms of product range.

3.2 Blow & Blow Process

The BB process is the oldest and remains still widely used in manufacturing of large and heavy containers such as wine or sparkling wine bottles. The gob is loaded into the blank mold, often via a funnel (Figure 3a). After loading, the mold is closed with a baffle and a settle-blow is applied from above through the baffle (Figure 3b). The settle-blow presses the glass gob deeper into the mold and down to the finish equipment, which basically consists of a neck-ring, a guide-ring, and a short plunger. On loading, the plunger is in upper position. In this very first step, the opening, sealing surface, and thread (if present) are thus formed before the bulk of the container itself, which represents an important difference with respect to the other forming processes.

In the current IS-machines, the loading speed of the gob is often so high that the finish is already formed at the gob-loading step, which would make the settle-blow unnecessary for the finish forming. This step is nonetheless maintained in the process to guarantee a constant heat transfer between the glass and the blank, from cycle to cycle, before counter-blow. During settle-blow, a vacuum can be applied through cavities in the molds to support the parison and finish forming. Some modern BB IS-machines work without a funnel. They control the switch between settle-blow and counter-blow by a valve in the baffle to exhaust the compressed air that is used for settle-blow.

After settle-blow, the baffle is quickly lifted, the funnel is removed, and the baffle settles again and closes the blank-mold completely. A counter-blow is applied from the down side through the formed finish, blowing the glass fully into the mold shape and forming the parison (Figure 3c).

This two-step blowing process with settle-blow and counter-blow on the blank-side causes an inhomogeneity in the container because of different contact times between the glass and the mold above and below the loading line. Such an inhomogeneity can be seen as a horizontal, optical streak in the body of the containers. It is called

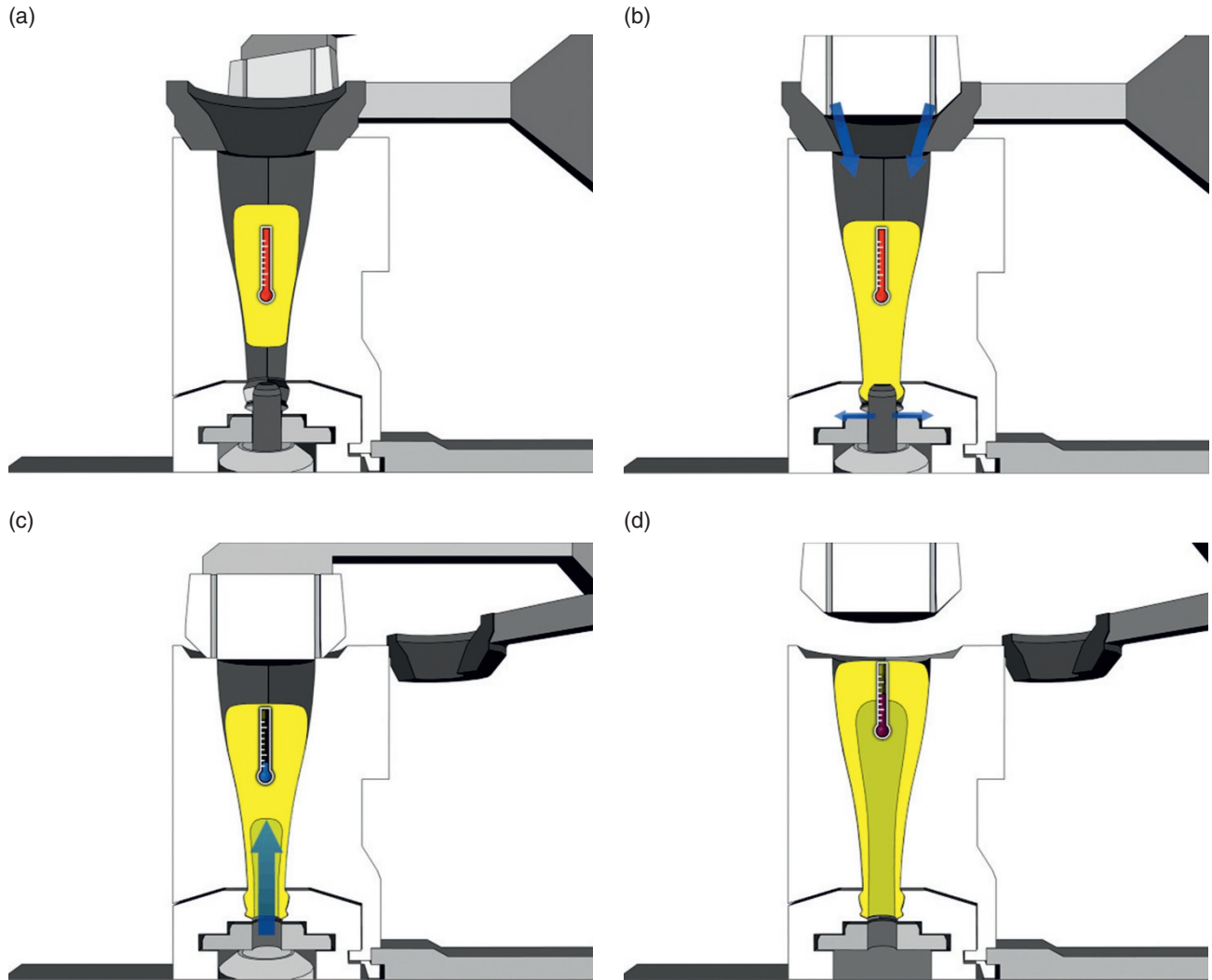


Figure 3 (a–d) Blow & blow process, blank-side.

settle- or feeder-wave and can be reduced in several ways, but not fully avoided. When looking at a final container, the existence or nonexistence of a settle-wave thus indicates whether or not the container has been produced with the BB process.

After the parison has been formed, the baffle is removed (Figure 3d), the mold opens, and the parison is transferred via the invert mechanism to the blow-side.

The final forming of the container is in principle the same for all three forming processes. The following description will thus apply to all of them. When transfer to the blow-side is over, the parison lengthens into the blow-mold as determined by its viscosity and the machine parameters. This causes the outside of the parison to be reheated by the heat stored in the hot inside and temperature to homogenize within the parison (Figure 4a). This reheat is essential to ensure that the container is to be precisely formed to its intended shape. The blow-mold is

then closed, leaving the finish outside. The invert-tongs open and the container is released from the invert. Directly after releasing, the blow-head with a blowing-tube is placed on top of the finish (Figure 4b). Through this blow-head, the final-blow is applied, giving the parison the final shape of the container (Figure 4c). Strictly speaking, the reheat ends when the final-blow is triggered.

After the container has been released by the blow-mold, a take-out grips it by its finish (Figure 4d) and places it over a dead-plate through which air is blown from below to cool it further. Finally the container is transferred via a pusher onto a conveyor belt.

3.3 Press & Blow Process

The PB process is used for wide-mouth containers of all weights, such as jars and baby-food containers. It differs



Figure 4 (a–d) Forming of the final container at the blow-side (same for all processes).

significantly from the BB process at the blank-side. After loading the gob (Figure 5), the blank-mold is closed fully by the baffle and a plunger presses in an upward movement the glass from below into the mold (Figure 5b). The plungers usually are made out of tungsten carbide (WC) or another hard metal to ensure a long lifetime. In contrast to BB-forming, the process causes the finish to be formed at the end of the blank-mold process (Figure 5c) and no disturbance such as settle-wave is introduced into the parison because it is formed by a single (smooth) motion at the blank-side. As in BB, the baffle is removed after the parison has been formed, the mold opens (Figure 5d), and the parison is transferred to the blow-side to get its final shape as described above.

3.4 Narrow-Neck & Blow Process

The NNPB process is mainly used for lighter containers such as beer bottles, small water and juice containers, and other lightweight containers. It is the most advanced forming process because it yields not only the highest machine speeds but also a homogeneous glass distribution in the final container. It is similar to the PB process in that the gob is not blown into the parison but pressed via a plunger. After loading the gob (Figure 6), the mold is closed fully by the baffle and a plunger smaller in diameter than in PB presses in an upward movement the glass into the mold (Figure 6b). The plungers are also made out of tungsten-carbide. As with PB, the finish is formed at the end of the blank-mold process (Figure 6c). Again, the baffle is removed after the parison has been formed,

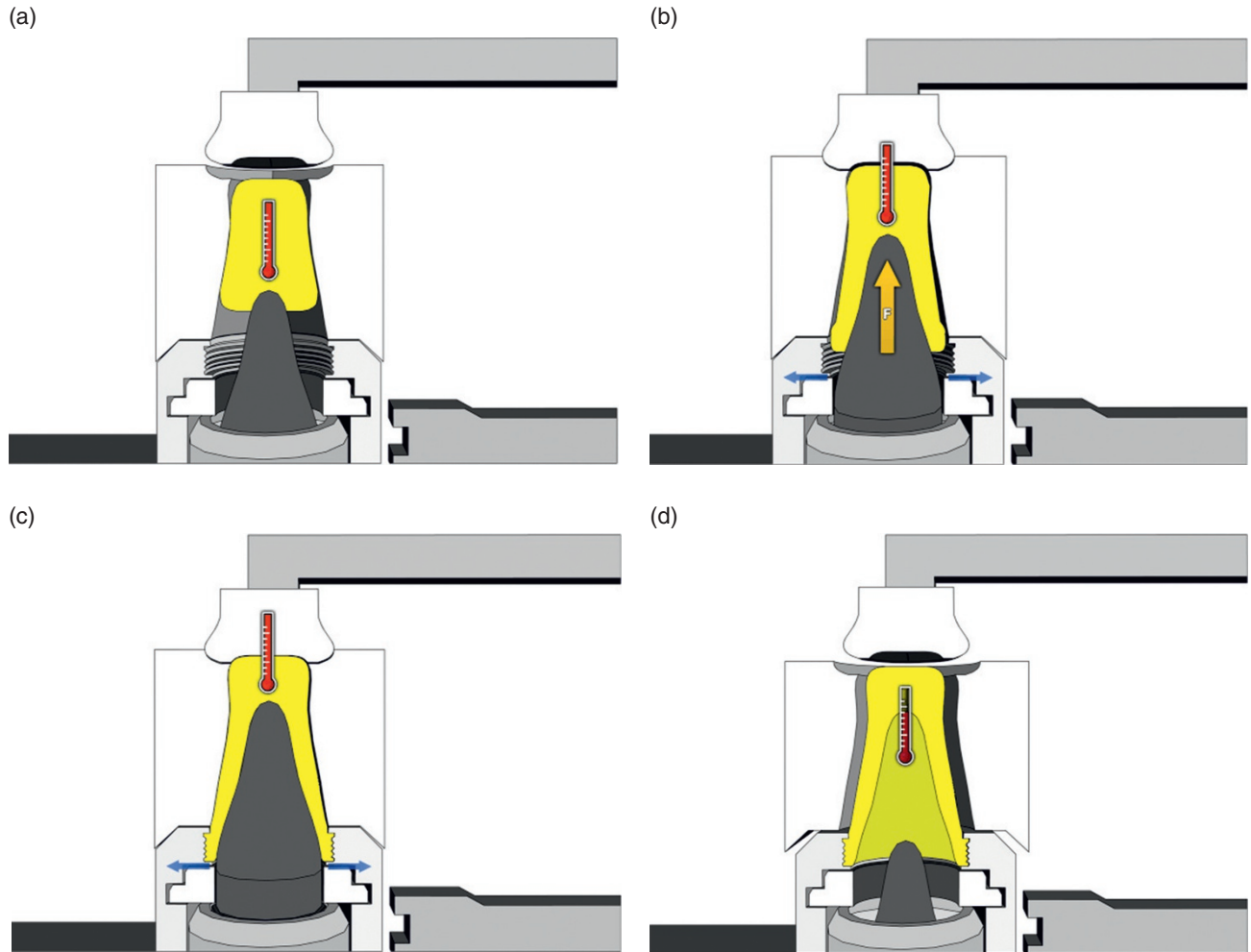


Figure 5 (a–d) Press & blow process, blank-side.

the mold opens (Figure 6d), and the parison is transferred to the blow-side.

Restrictions in usage of the NNPB process are due to the plunger dimensions and finish openings and the corresponding cavities pressed into the parison. The parisons are usually shorter for NNPB than for BB if the same final container shape is to be produced (e.g. a 0.33 l beverage bottle). Another significant difference between NNPB and BB is that the required gob temperature is from around 20 to 50°C higher in NNPB because of difficult pressing conditions. This difference in consequence leads to different thermal requirements during the process in terms of mold-cooling and reheat-timing.

4 Making of the Gob: Forehearth, Feeder, and Shears

Most forming processes take place at a viscosity of 10^2 – 10^4 Pa·s. Hence, for soda-lime-silica containers, the glass

needs to be cooled from melting and fining at ca. 1500°C and a viscosity of 10 Pa·s down to ca. 1050°C and a viscosity of 10^3 Pa·s. This quite demanding task is accomplished in the forehearth. The forehearth is directly connected to the working-end and ensures the required homogeneity of the glass while bringing it to the desired temperature and viscosity.

After the forehearth, a feeder enables glass-portioning and gob pre-shaping (Figure 7). It consists of a refractory tube and one or more plunger(s) that are moving periodically up and down. The tube is rotating to homogenize the melt in this final stage. With each upward stroke of the plunger, the glass stream is released from the shear blades in order to cut a gob without having a glass stream loaded on top of these shears. For a single-, double-, triple-, or quad-gob setup, the respective number of plungers operates simultaneously in the feeder, hence as many openings in the orifice ring are required. The final gob shape is influenced by the sizes of the orifice ring and plunger, and by the shape, height, and motion profile of the plunger.

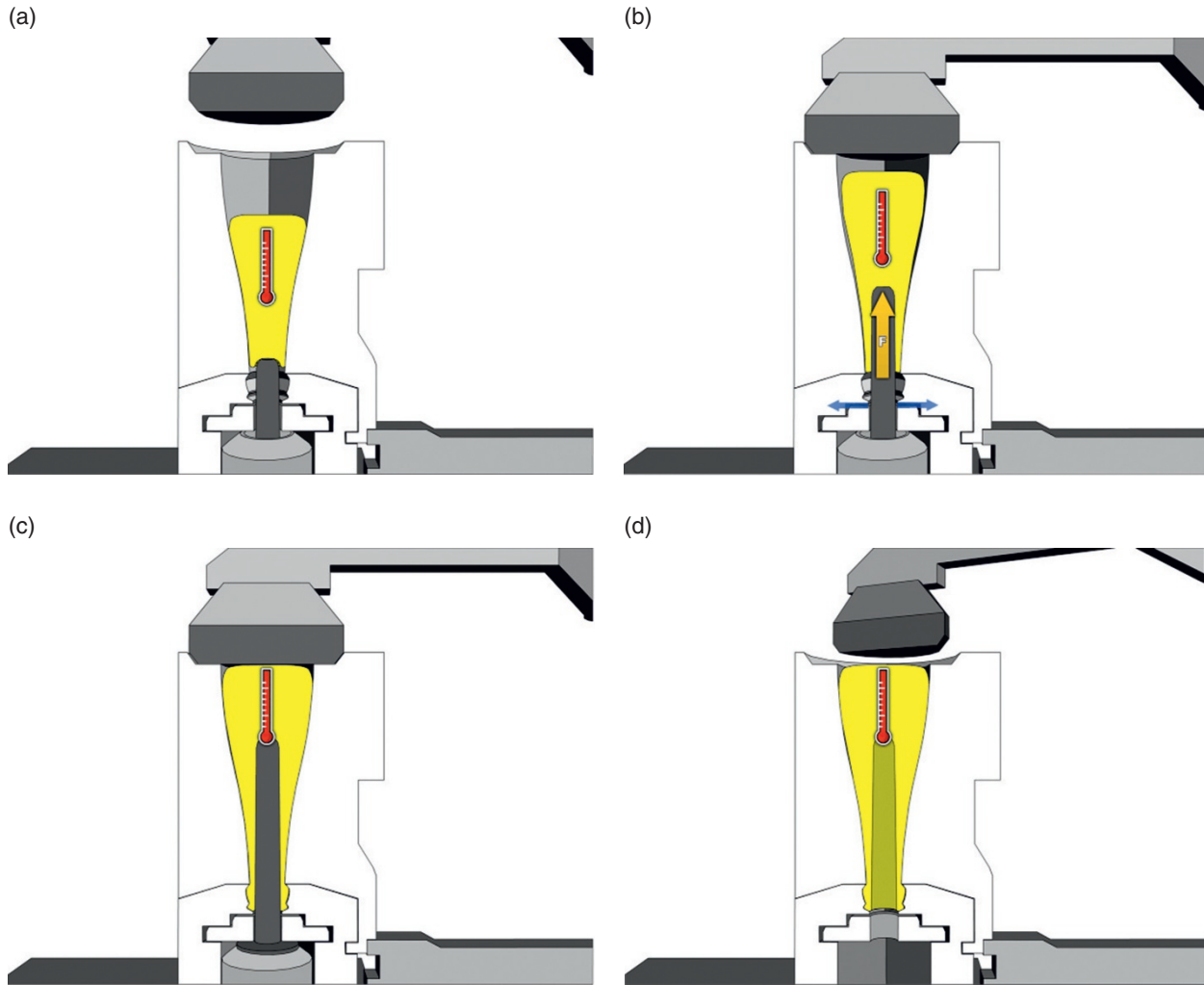


Figure 6 (a–d) Narrow-neck press & blow process, blank-side.

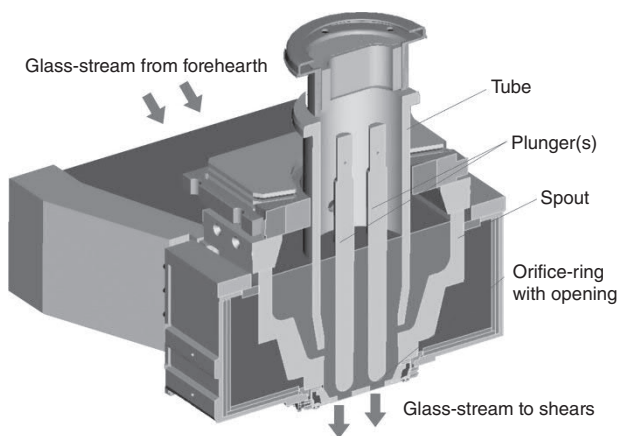


Figure 7 Cross section of a modern feeder (double-gob setup).
Source: Courtesy Bucher Emhart Glass.

The originally continuous glass stream is cut by the shears right after it has been “pre-shaped” by the feeder and plunger and has passed through the openings of the

orifice ring. The gob needs to be completely separated from the glass stream by the shears to prevent any glass fibers from being attached to it. Any misaligned or poorly operating shear will result in shear marks and, consequently, in defects in the final container. For shears, the materials most commonly used are steel (cheap, but short-lived) and hard alloys such as WC (more expensive, but long-lived). In all cases, the shears are cooled by a shear-spray, a mixture of water and cooling fluids.

5 IS-Forming Machine

5.1 General Principles

Rotational forming machines are nowadays used only in some rare cases. The principles of glass-container forming will thus be described for IS-machines, with which almost glass containers are made. Derivatives of the IS-machine such as the Emhart RIS and Heye H 1–2

machines have been developed in the past but are hardly in use any longer [9]. They work with two molds on the blow-side forming, which are loaded alternately. This approach is advantageous in terms of longer reheat and more homogeneous glass thickness distribution but is much more complicated, expensive, and prone to jamming.

In a narrow sense, IS-machines consist of a gob-distributor and delivery equipment, blank-side forming, invert, blow-side forming, and take-out and have several identical sections aligned in a row (Figure 1). The only differences between sections are the individual delivery (as different distances from gob-cut to mold need to be overcome) and the distance of the section to the annealing lehr. The differences in delivery distances cause different gob speeds and different gob arrival-times at loading and thus require different section-timings. The differences in distance to the annealing lehr may cause different containers temperatures at the hot-end coating and at lehr entrance. When entering the lehr, there is, for example, a difference of 50 K or more in surface temperature between containers from section 1 and from section 12, which are the farthest from the annealing zone.

The IS-machines in principle can be adapted to all three forming processes that have been mentioned earlier. To a certain extent the machines can be converted between a triple-gob setup to a quad-gob setup or, given another machine construction, from a triple-gob setup into a double-gob setup. How widely a machine can be adapted depends on different parameters, especially on the inner-section distance, which describes the possible center distances of the molds to each other within one section. The type of setup to be used depends on different parameters such as the size and weight of the container to be produced, desired machine speed, and portfolio of the respective glass-manufacturing plant.

5.2 The IS-Machine Families

The IS-machines can be separated into three groups:

- 1) Pneumatic-controlled IS-machines with angular mold-opening.
- 2) Pneumatic-controlled IS-machines with parallel mold-opening.
- 3) Servo-electric-controlled IS-machines with parallel mold-opening.

In the earliest types of IS-machines, all movements are controlled by pneumatic valves. The mold opening and closing is in an angular motion, which means that in a multi-gob setup at the blank-mold-side, the inner blanks are more widely opened than the outer blanks, causing difference in radiation between the glass and the open

blanks. At the blow-side, the inner molds are not opened as wide as the outer molds, which may lead to difficulties in machine accuracy and forming.

A significant step forward, therefore, was the introduction of pneumatic-controlled IS-machines with parallel mold-opening and closing. Here the mold-halves from the inner, middle, and outer cavity open in a parallel motion to each other. This leads to more comparable conditions between the molds of a given section. Furthermore, the parallel closing and opening is more precise, leading to a more reliable forming. In the color section of this Encyclopedia, a picture of a modern pneumatic-controlled IS-machine is shown.

The next logical improvement was to exchange the pneumatic-controlled movement for a servo-electric-controlled motion to take advantage of the enhanced stability, reliability, and precision of servo-electric drives. In this way, motions are much more easily cushioned and are gentler for the hinges, molds, and also for the glass itself. In the latest generation of IS-machines, mold opening and closing, plunger motion, invert, blow-head, take-out, pusher, and other parts are thus servo controlled.

The machine speed is a general parameter to describe the production performance for a given container. It is expressed as the cavity rate (C), namely the number of containers produced per minute (cpm) for each cavity considering the total numbers of cavities (N_S) of the IS-machine:

$$C = \frac{\text{cpm}}{N_S} \quad (5)$$

For a 12-section machine with a triple-gob setup and container output of 324 containers per minute, the cavity rate C is, for instance, $324/12 \times 3 = 9$. Hence, a 12-section IS-machine with a triple-gob setup producing 240 containers per minute is running a lower cavity rate than a 10-section IS-machine with the same triple-gob setup producing the same number of containers per minute. Highly efficient IS-machines can go up to cavity rates of 25 for small container sizes. This rate translates to production speeds of more than 700 containers per minute. In general, one can state that the higher the gob weight and the larger the container size, the lower is the corresponding cavity rate.

As illustrated in Figure 8 for 0.3-l beverage bottles, the performance of IS forming machines has steadily improved since their inception in the 1920s. In 90 years, one forming line has been producing 26 times more containers per minute. And in the same period the weight of such containers could be decreased from more than 300 to less than 170 g. These figures show vividly the very strong potential that this forming process had when it was invented.

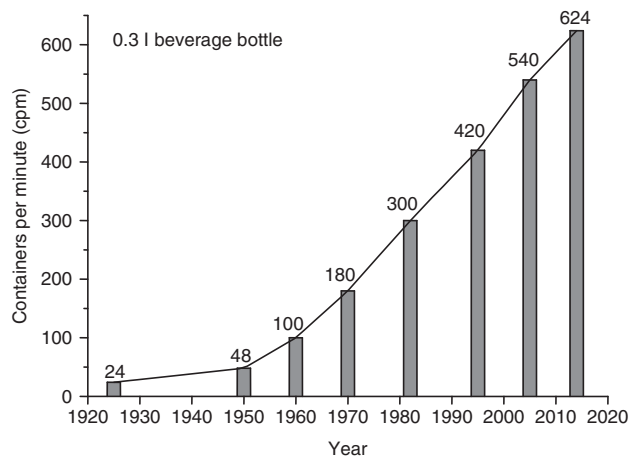


Figure 8 Performance increase of IS forming machines over the years in containers per minute.

5.3 Delivery Equipment

The delivery equipment consists of the gob-distributor (also called scoop), the trough, and the deflector. After the gob has been cut, it falls into the scoop which distributes the gobs to the different sections in the forming machine. The gobs slide through the respective troughs and then are redirected by the deflectors into the blank-molds. Although the delivery section looks like a simple part of the IS-machine, it bears considerable neuralgic points. The gob temperature decreases during the delivery but the upward side of the gob loses less heat than the side in contact with the metal delivery, which in some cases is in addition cooled and lubricated. Forming problems can thus happen if the gob acquires a non-uniform temperature profile.

The speed of the gob when it leaves the deflector is also an important parameter. When leaving the deflector, the gob is loaded into the mold. The higher the speed of the gob, the more beneficial it is for a good loading. Too slow a gob speed may lead to incorrect loading and hence to problems in the forming process or defects in the final container. In extreme cases, the gob is not fully loaded into the mold and the upper end of the gob is caught by the baffle. This leads to immediate failure of the respective section. The average gob speed at loading is between 6.5 and 7.5 m/s.

5.4 Blank-Side Forming

At the blank-side the three different forming processes come to play as explained in Section 3. Molds at the blank-side are usually made of laminar cast-iron. The glass gob is loaded into these molds and is formed into the parison. Because of process-sequence, the parison is formed upside down, the finish facing downward and

the bottom of the container upward before the invert leads to the proper upright formed final container. Upon forming of the parison, the mold is always cooled by air to allow fast heat extraction from the glass. As already explained, this is necessary to have a stable parison with a high enough viscosity after the mold has opened. If the parison is too hot and hence has a too low viscosity, it may collapse after opening the mold, causing section failure.

Different mold-cooling techniques are available. Most dominant are inside-mold cooling systems, where air is lead through channels in the mold either from below or from above and an older technique called stack-cooling. Here, fins are attached to the outside of the mold and the mold is streamed by air. This version is less efficient than inside mold cooling so that it usually leads to lower machine speeds.

5.5 Invert and Reheat

After forming of the parison, the blank-mold opens and the parison is transferred via an invert to the blow-side. The invert consists of an invert-arm in which the finish equipment with neck-ring and guide-ring is fixed. As soon as the blank-mold opens and invert takes place, the so-called reheat starts. During the blank-side process, the glass-surface has been cooled down, especially through the contact with the molds and blowing air. The glass viscosity rises in this way, which is necessary to give the parison a certain rigidity to move it without deformation. After having been released from the blank-mold, the outer parts of the parison get reheated from the hotter inner part through thermal conduction, which is in fact needed to lower again surface viscosity before the last forming step that will give the container its final shape.

5.6 Blow-Mold Forming

The forming of the final container in the blow-mold is from a mechanical point of view identical for all three forming processes (BB, PB, and NNPB) as explained in Section 3.

As with parison forming at the blank-side, final blowing at the blow-side can also be aided by vacuum. A main task for the blow-mold is to extract as much heat from the container as fast as possible to increase its viscosity, stabilize its shape, and avoid deformations during take-out and transport of the container after it has been released from the blow-molds. Because of this need to extract large amounts of heat in a short time, blow-molds often are made out of aluminum-bronze, which has much higher heat conductivity than cast-iron, hence allowing faster heat removal from the container.

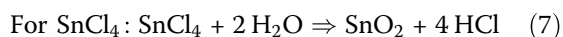
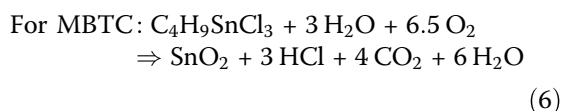
A picture of a triple-gob setup in the color-section of this Encyclopedia shows the parisons just having arrived at the blow-side and the final containers just having been removed from the blow-mold and placed over the dead-plate by the take-out.

6 Hot-End Handling, Hot-End Coating, and Annealing

The conveyor belt transports the container to the annealing lehr for stress-relaxation. Once the container has left the IS-machine, a first inspection often takes place with cameras that record the infrared images of the hot containers. From these images, defects can be identified and immediate corrections of the process can be initiated. This is very beneficial as the feedback between defects and applied corrections is direct and without the time delay that would occur if the container were first annealed and then inspected.

Before entering the annealing lehr, the outside body (not the finish) of the containers receives a hot-end coating of a 5–15 nm thickness. Even so thin, the hot-end coating serves different important functions. It first saturates the highly reactive surface bonds that are present at the surface of the new glass container. It also provides a surface suitable for good adhesion of the cold-end coating, which is applied later. Furthermore, it may slightly increase the strength of the container by disabling surface flaws that have been introduced during the forming process.

As precursor for hot-end coating most frequently used is monobutyltin-trichloride, $C_4H_9SnCl_3$ (MBTC) or tin-tetrachloride, which both gives rise to a SnO_2 coating on the container. The process is chemical vapor deposition under air at atmospheric pressure (atmospheric CVD) and is supported by the moisture of the air. The reactions that take place are:



Other precursors based on titanium or titanium-silicium are also in development to yield a TiO_2 or TiO_2 - SiO_2 coating. As explained, after forming and hot-end transport, the containers from different sections experience different cooling whereas the surfaces of a given container cool faster than its bulk, the rate being higher for the outer than for the inner surface. These differences create tensile stresses in

the container, which can lead to spontaneous breakage. Containers are thus reheated in the glass transition range in a continuous-annealing lehr long enough to ensure complete stress relaxation. The annealing times depend on the size of the containers, but are typically between 45 and 60 minutes. The containers can then cool down to room temperature homogeneously.

7 Cold-End Handling and Inspection

When they leave the annealing lehr, containers have a temperature between 80 and 120°C. They are coated a second time in a spray process. The main purpose of this cold-end coating is to protect the container against scratches upon further handling and later at the filling line. Usually a polyethylene wax is used to decrease surface friction, hence making the containers less susceptible to scratches when being handled or touching one another. The cold-end coating also serves to provide a surface suitable for good adhesion of the label, which is usually fixed at the filler.

After application of the cold-end coating, another inspection takes place in a highly automated way such that additional inspection by human eye is applied only in rare cases. Most inspection systems are based on various sophisticated optical systems, each checking for a certain type or group of potential defects that include flaws, scratches, cracks, blisters, seeds, loose or stuck glass particles, or dimensional errors of the container. Because special attention is paid to the finish of the container, mechanical inspection systems are, for instance, applied for testing that it is free of obstacles. Finally, random checks are made offline, e.g. to check that the strength exceeds definite values that depend on the kind of container. For impact strength, usually a minimum lot-size of 30 containers is tested on a shift, daily or some other regular basis, depending on the container made and plant procedures. The container is hit by a pendulum of a certain weight – depending on the chosen specification and domain of the container – in a well-defined matter until it breaks. As for the burst pressure strength, which is especially relevant for carbonated liquids such as sparkling wine, water, and champagne, the container is filled with water and its pressure is increased until breakage. Also here, due to the Weibull-characteristics of brittle materials, a minimum of at least 30 containers should be tested. After inspection, the containers are pelletized, wrapped, and prepared for shipment.

8 Perspectives

With the introduction of PET and other plastic containers, the glass industry has experienced a severe loss in market share for certain types of products such as juice, water, and milk. After years now the market seems balanced and the container-glass industry could maintain a quite stable production level of ca. 65 million tons worldwide, which amounts to ca. 200 billion containers in 2012.

Recently, however, disadvantages of plastic containers have been recognized. Because of the leaching of endocrine-active substances, phthalates and other substances into the container content [10, 11] and the dispersion of plastic waste on land and especially in the oceans [12], glass might even be able to gain more acceptance from the consumer. Here, glass can play out its strengths as, among other positive aspects, it is fully inert and can be 100% recycled. Furthermore, glass in a landfill does not pose any threat to the environment as it degrades to the components it was made of.

Nevertheless, glass has also its well-known drawbacks and a positive future of container glass strongly depends on the capabilities to overcome them. First, there is the fact that glass containers are energy-intensive to produce. Emission control, CO₂-trading, rising energy costs, and other environmental regulation force the glass-industry to push limits farther (Chapter 9.7). As processes are already highly optimized, there are no more “low-hanging fruits.” Although the effort that has to be made financially and risk-wise increases exponentially with the possible benefit that can be gained, the container-glass industry is aware of the need of innovations. The increasing number of batch and cullet preheaters or the latest concepts to

allow heat recovery for oxy-fuel fired furnaces illustrate the kind of efforts made to keep shifting the limits.

Other weak points are the fact that glass containers are brittle and mostly regarded as heavy. In specific instances, however, weight is considered a positive aspect of glass packaging. For example, think of the smooth texture, the reassuring heft, and the feel of value when lifting a glass bottle of wine or perfume. Nevertheless, many investigations have been carried out to decrease the weight of glass containers while increasing their strength. Coatings based on silica-sol-gels (Chapter 8.2) can, for instance, increase the strength of glass containers by 20% or more.

Besides, most impressive are current developments which aim at thermal strengthening of containers. After forming, the containers are reheated and then cooled from both inside and outside much faster and in a much more controlled way than in an annealing lehr. In this manner, compressive stresses at the inner and outer surface are introduced, which significantly increase the strength of the glass so that containers can be lightweighted further or be reused. The key to this development is to control the cooling very precisely and to adjust the balance between compressive stresses at the surface and tensile stresses in the bulk of the container (Chapters 3.7 and 3.12).

Innovations are also targeted in the field of glass-contact materials. Coatings for enabling a full non-swabbing production of all types of containers are investigated, but this task is still unsolved. Furthermore, it is highly desirable to avoid all lubricants that are currently used in shear-, trough-, and mold-lubrication. This would allow a full “dry-gob” delivery that would give considerable advantages over current process.

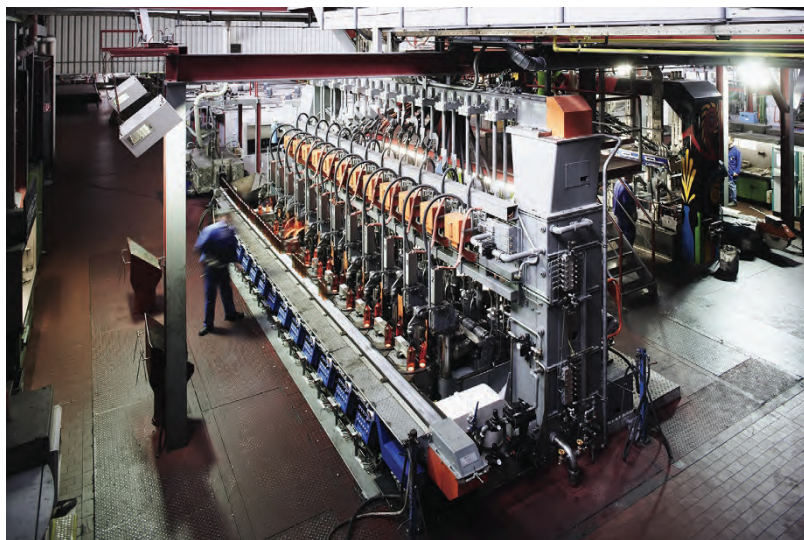


Figure 9 A modern pneumatic-controlled 12-section double-gob individual-section machine; on the left, the conveyor belt evacuating the newly blown bottles (courtesy Bucher Emhart Glass).



Figure 10 Parison just before blow-mold closing and final container on the blow-mold-side. Source: Courtesy Bucher Emhart Glass.

Concerning the IS-machine itself (Figures 9 and 10), a significant improvement would be to ensure a more precise and controlled forming process and, hence, a more homogeneous wall-thickness distribution in the final container. This could, for instance, be achieved by a direct gob-loading without the need of a delivery or by a forming process, which would allow a more precise reheat to have a more homogeneous final container forming. Because cost competition with alternative packaging is one of the biggest drivers and deciders for innovations, however, all the aforementioned approaches and concepts will have to distinguish themselves not only by their technical feasibility but also by their economic efficiency.

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1.6

Continuous Glass Fibers for Reinforcement

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1 Introduction

Numerous examples of the use of glass drawn as fibers can be found throughout history. The early Egyptians wrapped glass fibers over clay vessels and then fused them to form glass vessels. Venetian glass blowers in the sixteenth and seventeenth centuries used glass fibers to decorate elaborate glass articles. Glass fibers were even used as fabric elements in fashion garments in the late nineteenth century. It was in the mid-1930s, however, that two key developments created the means for glass fibers to become the base for a new industry based on composites—organic polymers reinforced with glass fibers, more commonly known as glass reinforced plastics, or GRP. The first was improvements in the process of manufacturing glass fibers at the Owens-Illinois Glass Company so that commercial fibers could be made in a multifilament strand form that met basic material handling requirements for downstream processing into composite structures [1]. The second was the development of polymeric resin systems by DuPont and others that could be combined readily with glass fibers. These glass-fiber reinforced polymer–matrix composites offered key material advantages over conventional metallic materials, including light weight, stiffness, and strength, and resistance to corrosion and fatigue.

Today, glass fibers have become the most widely used and cost-effective reinforcing fibers in the arena of commercial polymer–matrix composites. Early melt spun processes producing discontinuous fibers have evolved to today's large-scale direct melt continuous fiber-forming operations. One of the first needs for continuous fibers was for insulation of electrical wires for high-temperature applications, leading to the development

of a new glass composition based on a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ system that met the electrical requirements and subsequently became known as E-glass. Because these fibers also exhibited excellent mechanical properties and could be made in relatively high-volume manufacturing operations, the original E-glass compositions rapidly spread into many composite applications. Today, the glass fiber reinforcement spectrum has grown to include an increasing array of specialty glass compositions that are targeted for key expanding markets in electronics, transportation, corrosion, construction, and in energy management.

Prior to 2000, most major glass fibers manufacturers were concentrated in North America and Western Europe. Today, fiberglass production facilities are flourishing in China and beginning to spread to other regions of the world to satisfy a constantly growing demand of GRP. It is the intent of this overview to provide insight into the technology that is associated with the continuing success of glass as a reinforcing fiber. Fiberglass technology associated with both material characteristics and manufacturing processes are described at a high level.

2 Commercial Glass Fibers

2.1 History of Fiberglass Development and Glass Chemistry

2.1.1 Fiber Types

Reinforcement glass fibers can be broadly divided into two categories – general-purpose and premium special-purpose fibers. The former are known as E-glass and subject to specific compositional ranges as defined by recognized standards such as ASTM D578 [2]. Historically, E-glass fibers have been predominant in the commercial production of fiberglass products for use as

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J. Thomason, The University of Strathclyde, Glasgow, Scotland, UK

reinforcements in various industrial polymer–matrix composites applications. Other types of fibers that have been used in special purpose and low-volume applications include S-glass, R-glass, D-glass, ultrapure silica fibers, and hollow fibers [3].

Continuous glass fibers for composite reinforcement have been categorized by the specific properties required for end-use applications (Figure 1). An overview of the historical timeline of the development and commercial use of these major glass types is represented on the horizontal axis. Further detail on the typical oxides and oxide ranges, physical and mechanical properties, and processing-related properties that are characteristic of the major glass types used in glass fibers are listed in Tables 1 and 2, respectively. More specific examples of recent developments in the areas of D-, S-, and R-glasses are also included.

2.1.2 E-Glass

First commercialized in the late 1930s [1], E-glass fiber remains the most widely used class of fiberglass for GRP materials [3, 4]. Its composition primarily lies within the ternary $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system with B_2O_3 and F_2 contents that vary from 0 to 10 wt % and 0 to 2 wt %, respectively. For much of its history, E-glass fiber production incorporated B_2O_3 in commercial compositions at levels of 7–8 wt %, which provided an optimal balance of melting and fiber-forming characteristics, mechanical properties, and electrical properties. Over time, however, increasingly restrictive environmental emissions requirements for particulates have been driving costs up for emission control systems. Countries such as Canada and Norway were leaders in the push to improve environmental conditions, leading to the introduction of the first boron-free commercial glass fibers. These glasses had in addition excellent corrosion resistance under strongly acidic conditions [7]. They have been designated as E-corrosion resistant (E-CR) glass fibers in the late

1970s. Over time, optimizations of minor oxide components such as TiO_2 , ZnO , and MgO served to improve their cost and manufacturing efficiencies while also providing proprietary regions in the compositional space as their use was growing rapidly.

In key areas outside of the corrosion markets, however, there was resistance to move to low-boron compositions. The electronics industry, dominated by E-glass fabrics used in printed wiring boards (PWB), relied on the unique value set of electrical consistency, dimensional stability, processing predictability, and low cost provided by conventional E-glass over many years and resisted any change in the E-glass standards. The aerospace industry also resisted the change, based on a well-defined history of performance of conventional E-glass and a desire to minimize any risk, however small, which might be incurred by what was perceived as a significant material change.

As a consequence of these developments, commercial E-glass fibers today fall into two major categories: low or zero B_2O_3 levels for general reinforcements, and higher B_2O_3 levels (>5%) for electronic and aerospace applications. The distinction between these categories is clearly defined in ASTM D578 [2].

2.1.3 C-Glass

Other reinforcement fibers containing B_2O_3 were developed in the early 1940s as C-glass, which has limited use as discontinuous fiber products for roofing materials. Continuous boron-free variants of C-glass fibers with improved chemical resistance to acids came to market in the mid-1960s. The composition is primarily composed of Na_2O , CaO , Al_2O_3 , and SiO_2 . The absence of boron resulted in improved acid resistance; the mechanical performance (strength and modulus) of C-glass fiber is inferior to those of both E-glass and E-CR glass, however, so that applications of this glass in the reinforcements industry have been limited to nonstructural uses

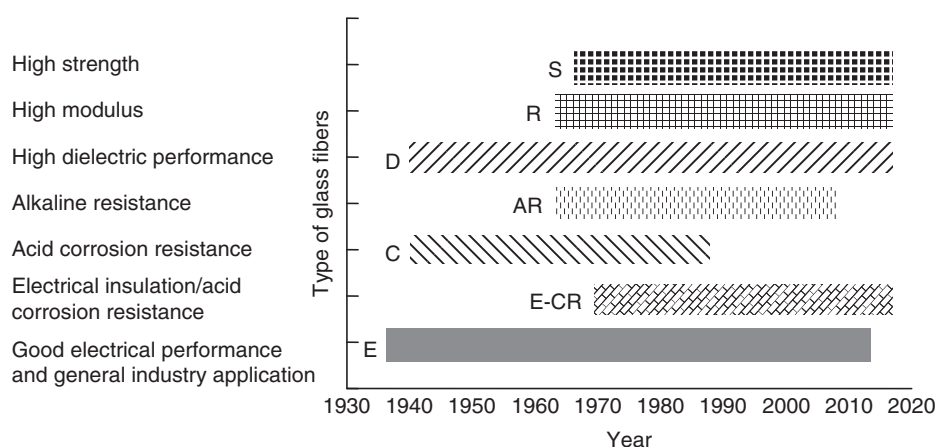


Figure 1 History of commercial continuous fiberglass development (most active period in development shown and beyond 2015 most intensive research areas projected are S, R, and D glass fibers) and standard nomenclature/classification based on their key properties used in commercial applications [4].

Table 1 Composition of glass fibers found in literature and/or commercial market [2–6].

Fiberglass	SiO ₂ (wt %)	Al ₂ O ₃ (wt %)	MgO (wt %)	CaO (wt %)	SrO (wt %)	BaO (wt %)	B ₂ O ₃ (wt %)	R ₂ O (wt %)	F ₂ (wt %)	ZrO ₂ (wt %)
E including E-CR	52–62	12–16	0–5	16–25	—	—	0–10	0–2	0–2	—
C (China) ^a	67.0	6.2	4.2	9.5	—	—	0	12	<1	—
C (Europe)	53–65	3.8–16	2.4–3.8	14–16	—	—	3–6	7–9	0.3	—
A ^b	72–72.5	1–1.5	2.5–3.8	9–10	0	0	0	13–14	0	0
AR ^c	61–71	0–3	—	<5	—	—	0	<18	—	16–22
D	72–76	0–1	—	<1	—	—	20–25	<4	—	—
D (derivative I)	52–60	10–18	0	4–8	—	—	20–30	Trace	0–2	—
D (derivative II)	50–60	10–18	1–6	2–5	1–9	1–5	14–20	<1	0–2	—
D (derivative III)	60–77	9–15	5–15	0–11	—	—	5–13	0–4	0–2	—
R	58–60	23–26	5–6	9–11	—	—	0	—	—	—
R (derivative)	56–65	12–20	6–12	8–16	—	—	0–2	0–2	—	0–2
S	64–66	24–25	9.5–10	<0.2	—	—	0	<0.3	—	—
S (derivative)	55–65	23–26	9–15	—	—	—	0–4	<1	—	—

^a C-Glass (China) is specified by Chinese Standard JC583-1995.

^b A-glass fiber (close to window glass composition) has low hydrolytic resistance, sensitive to moisture attack at room temperature, and, hence, is inappropriate for GRP composite applications.

^c ZrO₂ in AR-glass is specified by ASTM C1666/C1666M-08.

such as nonwoven fabrics for corrosion liners, building insulation materials, sewage pipes, etc. For many years, C-glass served as the primary form of glass fiber for low-cost regions of the world in emerging markets, at present less than 10% in volume relative to E-glass fibers produced each year in China. The balance of mineral components with no need for a boron source provided a glass fiber based on widely available raw materials that could be easily manufactured in low-technology operations. Hence, these properties led to the broad commercialization of C-glass as a low-cost substitute for E-glass fibers in regions where modern fiberglass furnace technology was not commonly available. Many early fiber producers in China used C-glass. The trend today, however, is to move away from C-glass fibers to the production of E-glass and other high-performance fibers. Little development has occurred since the mid-1980s, and C-glass fibers represent less than 5% of fibers used in glass fiber reinforced composites today.

2.1.4 AR-Glass

As named for its alkali-resistant properties, AR-glass fiber was invented in the mid-1960s and first commercialized by Pilkington Brothers in the United Kingdom in the early 1970s under the trade name Cem-Fil®. It was presented as a glass fiber option for reinforcing concrete structures. The glass chemistry was actually developed by a chemist at the Building Research Establishment and licensed to

Pilkington by the National Research and Development Corporation, leading to its initial commercial application. The glass chemistry is primarily comprised of Na₂O, CaO, ZrO₂, and SiO₂ with a small amount of Al₂O₃. The higher Al₂O₃ found in most commercial glass fibers results in lower ZrO₂ solubility. Unlike E-CR fibers, AR-glass fiber offers high resistance to alkaline corrosion as well as to acid corrosion. This resistance is attributed to the formation of a protective layer rich in ZrO₂ on the fiber surface in corrosive media. Because of the relatively high Na₂O and low Al₂O₃ levels, the fiber modulus and tensile strength are lower than for E-glass fibers despite the high concentration of ZrO₂. The overall higher production and material cost of AR-glass limits its utility to challenging fiber applications in cement reinforcement. Current developments are focused on increasing ZrO₂ solubility to improve further corrosion resistance and to improve melting and fiber-forming costs.

2.1.5 D-Glass

An optimum combination of dielectric constant (D_k) and dissipation factor (D_f) over a frequency range of 1 MHz to 40 GHz is provided by pure SiO₂ glass. This property set is of particular utility in the field of PWB and electronic chips and circuitry, driven by the dramatic growth of computers and consumer electronics. It is to allow production of glass fibers approaching the performance of SiO₂ glass in a reasonable commercial process that

Table 2 Typical properties of fiberglass found in literature and/or commercial market [3, 4, 6, 7].

Fiberglass	Fiber density ρ (g/cm ³)	Pristine strength σ_f (GPa)	Sonic modulus E (GPa)	Dielectric constant D_k (1 GHz)	Coefficient thermal expansion CTE (10 ⁻⁶ /°C)	Softening temperature T_{soft} (°C)	Liquidus temperature T_{liq} (°C)	Forming temperature T_F (°C)	Melting temperature T_M (°C)
E (including E-CR)	2.60–2.65	2.8–3.5	70–85	6.6–7.1	5.4–5.9	846–920	1080–1220	1180–1282	1345–1460
C (China)	2.53	2.6	65	7.5	8.4	—	1095	1217	1469
C (Europe)	2.52	3.3	69	—	—	750	1127	1157	1400
A	2.46	3.0	62	10.6	9.0	704	996	1185	1443
AR	2.68–2.78	3.2–3.7	73–77	—	—	820–847	1049–1192	1237–1247	1430–1467
D	2.11–2.14	2.4–2.5	52–55	3.8–4.0	3.1	771	953	1410	>1600
D (derivative I)	2.30	—	55–59	4.7–5.0	3.3–3.5	850	997–1270	1314–1382	>1550
D (derivative II)	2.30	2.5–3.1	57–64	5.4–5.8	4.0–4.9	830–875	1000–1054	1174–1298	1384–1502
D (derivative III)	2.34–2.42	3.3–4.1	73–82	4.8–5.6	4.1	944	1083–1287	1244–1388	1465–1641
R	2.55	4.1–4.5	85–87	6.4	3.3	952–975	1330	1410	—
R (derivative)	2.55–2.62	3.7–4.5	85–90	6.5	4.5–5.0	920–980	1170–1238	1265–1300	1468–1550
S	2.45–2.49	4.7–5.0	87–88	5.4	1.6–2.8	1030–1056	1439–1471	1424–1448	1620–1640
S (derivative)	2.53–2.56	4.2–4.8	86–95	—	2.8	920–968	1320–1450	1283–1450	—

Note: CTE values correspond to temperature range from room temperature to 300 °C; T_{soft} corresponds to glass viscosity of 10^{7.6} Pa·s as typically used in fiber glass production; T_F is defined by melt viscosity of 10² Pa·s as a reference temperature for drawing fibers; T_M is defined by melt viscosity of 10 Pa·s as a reference fining temperature to be reached in the industrial melting process.

D-glass has been designed. The earliest D-glass fiber composition was essentially a binary mixture of SiO_2 and B_2O_3 . Although D-glass fiber has significantly lower processing temperatures than pure SiO_2 , these temperatures are still substantially higher than those of E-glass fibers for PWB yarns. Melting temperatures are greater than 1600°C and fiber drawing temperatures greater than 1400°C . Recent developments have widened the D-glass fiber composition space by introducing Al_2O_3 , alkaline earth oxides (MgO , CaO , BaO , and SrO), and/or small amounts of Li_2O (Table 1) [5]. These composition modifications significantly lowered glass melting and fiber drawing temperatures, providing more favorable production costs and improved commercial viability. The drawback is a modest increase in D_k and D_f relative to the original D-glass composition. To achieve target product electrical properties, PWB laminators can use different resins with lower D_k and D_f . It is also possible to change the PWB layer stack and layout to meet target electrical performance for high-end PWB substrates. Another development is to lower the coefficient of thermal expansion of the glass fiber to improve PWB substrate thermal stability. This reduces thermal fatigue susceptibility and leads to a reduction in thermally induced cracking on chips. Continuing improvements in D-glass compositions keeps glass fiber at the forefront as a key element of choice in smaller, faster, lighter, and more electrically dense electronic components.

2.1.6 S-Glass

Known as S-glass, fibers primarily composed of MgO , Al_2O_3 , and SiO_2 were first developed in the late 1960s for high-temperature and high-strength applications and further expanded into military ballistic protection applications in the 1970s [6]. Because of high liquidus temperature (1470°C), fibers must be drawn at temperatures significantly greater than 1500°C to avoid fiber breakage caused by crystallization as the fibers are formed. This property attribute means that S-glass fibers must be drawn in a much lower viscosity range than that of typical commercial fibers (Section 3.2). The challenges of this severe process limit the number of product forms and result in very high costs that have limited the commercial utility of S-glass fibers to high-performance markets such as aerospace and military applications where strength and weight combined can justify a premium over other materials. There are no large-scale commercial production platforms in the S-glass family. Derivatives of S-glass have been investigated through introduction of small amounts of B_2O_3 and other oxides (Li_2O , CeO_2) to improve glass melting and fiber-forming performance. To date no large commercial-scale production has materialized.

2.1.7 R-Glass

For military applications, R-glass was first developed in the mid-1960s within the quaternary $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ system. In its original chemistry, its production, like that of S-glass, was limited because of the requirements imposed by its high melting temperature. The addition of CaO to the S-glass ternary system improved the processing conditions required to make glass fibers while still providing a high level of strength, but conditions were still more challenging than E-glass. Developments centered around the R-glass compositional range increased in the mid-00s, driven by the needs of wind-turbine blade producers who required longer blades with higher-modulus glass fibers to reduce the unit cost of electricity generation. Most of the improved technology made is based on reducing glass melting temperature while increasing fiber modulus, which has been realized by optimization of mixed alkaline earth oxides (MgO/CaO). As a result, large-scale furnaces and large direct-draw bushing operations are possible. [4]. These developments have provided a balance of mechanical performance, cost, and large-volume production capability that is in good alignment with the scale of production and cost of energy drivers in the wind-energy composites market. The speed at which these new high modulus fibers have been put on the market is unprecedented in glass-fiber history.

2.1.8 Glass Type Summary

With its derivatives such as ECR glass, E-glass continues to dominate global commercial sales of glass fibers for reinforcement applications. The unique combination of mechanical properties, weight savings, and durability combined with a wide array of available form factors in the form of fiber diameter, strand size, resin compatibility as delivered by sizing chemistry, continuous or chopped forms, and cost-effectiveness make E-glass fibers by far the best value for designing and manufacturing high-performance composites on a large scale. In parallel with ongoing improvements in E-glass performance, technology developments associated with high-performance fibers, i.e. re-engineered or derivatives of S-glass, R-glass, and D-glass will continue to be key focus areas in the future. These technologies serve to expand the growth of glass-fiber reinforcements in transportation, aerospace, both traditional and renewable energy, and safety and security markets. These added technology options in glass fiber address light weight, high strength and high modulus [4, 6], improved durability, and improved electrical performance such as low signal loss and high-speed communication in the PWB industry [5].

In developing new glass fibers, a fundamental understanding of glass network structures and glass properties

for both performance and processing are critical. In boron-containing glasses such as E- and D-glass, speciation of boron in the network, i.e. $\text{BO}_4 \leftrightarrow \text{BO}_3 + \text{NBO}$ (non-bridging oxygen), is affected by both melting temperature and glass composition [8]; in turn, melt viscosity and glass dielectric property are affected. Besides the speciation of silicate network affected by modifying oxides [9], all commercial silicate glass fibers contain alkaline earth oxides and alumina; an in-depth understanding of composition effect (particularly high field strength metal oxides, MO_x) on speciation of aluminum, i.e. $\text{MO}_x + \text{AlO}_y \leftrightarrow \text{MO}_{x-1} + \text{AlO}_{y+1}$ ($x = 7, 8$ and $y = 4, 5, 6$) [9–11], can assist in glass design for achieving better glass mechanical properties and facilitating melting and fiber-forming processes.

2.2 Major Fiberglass Producers

Worldwide production of E-glass fibers reached about 7.3 million metric tons ($7.3 \cdot 10^{12}$ kg) in 2018 and is projected to grow continuously. The expansion of E-glass fiber production capacity is expected to occur in parallel. Fiberglass companies can be ranked by total annual sales in volume whereas total production capacity of each company is much more difficult to find in the public domain. The current top 10 fiberglass producers globally based on sales in past 5 years are listed in Table 3. The largest rate of expansion has taken place in China, where newly built furnaces in recent years ranged from annual capacity of 30 000 metric tons to 120 000 metric tons per furnace.

3 Manufacturing of Glass Fibers

3.1 Primary and Secondary Processes

The production of glass fibers encompasses a wide range of processes, from raw-material sourcing, batch weighing and mixing, batch-to-glass melting and fining, fiber drawing with the application of a water-based organic sizing, to finally drying. Much of today's glass-fiber production for reinforcements incorporates direct processing wherein the finished product, whether wound into a continuous spool of fiberglass strand or chopped directly after the fibers are formed and coated with sizing, is produced in one step as a part of the forming operation. Secondary downstream processes are still in use for some applications and may include twisted yarn on bobbins, roving packages made by assembling collections of smaller strands into larger strands, fibrous mats made from chopped or continuous strands bound together by mechanical or chemical binders, and chopped products for some specialty applications. The general process is sketched in Figure 2. For E-glass fiber production, combustion technology is moving from natural gas–air or oil–air to natural gas–oxygen to achieve better energy transmission efficiency. Where C-glass fiber is still in production, the use of syngas remains prevalent for furnace and combustion systems because of lower capital costs. For both types of fibers, electric boost technology has increased in utilization for energy efficiency and for lowering top firing and hence lowering the crown temperature of the furnace to prolong its life. The following sections briefly discuss some of the key areas of glass melting/fining, fiber drawing, and sizing chemistry design.

Table 3 Top 10 fiberglass producers (2008 – 2013).

Name	Headquarter	Sales ranking	Major market	History
Owens Corning (OC)	US	1	Construction/Transportation	Since 1938
China Fiberglass Co., Ltd. (Jushi)	China	2	Construction/Infrastructure	Since 1993
PPG Industries, Inc. (PPG) ^a	US	3	Transportation/Renewable energy/Electronics	Since 1945
Chongqing Polycomp International Corporation (CPIC)	China	4	Transportation/Renewable energy	Since 1986
Johns Manville (JM)	US	5	Construction	Since 1958
Taishan Fiberglass Inc.	China	6	Renewable energy/Construction	Since 1983
Nippon Electronic Glass (NEG) ^a	Japan	7	Transportation	Since 1976
3B – Binani (3B)	India	8	Automotive	Since 1996
Sichuan Weibo	China	9	Transportation/Infrastructure	Since 1996
Taiwan Glass Group (TGG)	Taiwan	10	Construction	Since 1990

^a PPG sold its Fiber Glass business to NEG in 2017, which makes NEG's rank No. 3.

Source: Fiber glass market study, PPG, 2014.

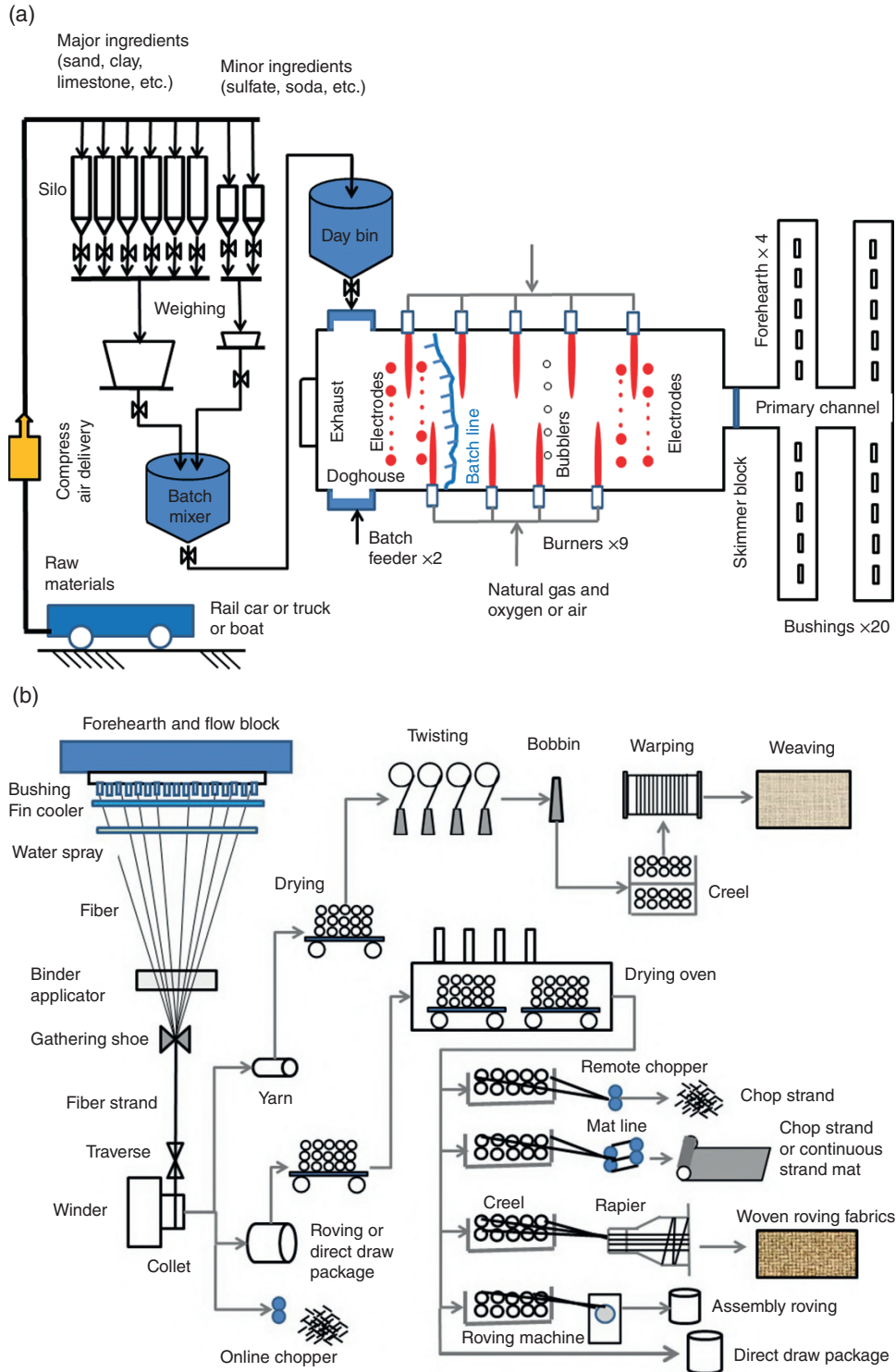


Figure 2 Schematic illustrations of continuous fiberglass manufacturing processes: (a) batch operation, batch melting/glass fining, and glass delivery to bushing positions, common burner locations used in the primary canal and forehearth (not shown) and (b) steps in fiber drawing and downstream processes. Source: Fiber glass market study, PPG, 2014.

3.2 Glass Melting and Fining

Commonly used raw materials for E-glass fiber include sand (SiO_2) as the primary silicon source, kaolin or china clay consisting of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) as the primary source of aluminum, limestone (CaCO_3) or quicklime (burnt lime, CaO) as that calcium, and boric acid (H_3BO_3) as that of boron. More complex minerals are often used in place of or in combination with these major components to manage cost, improve melting performance, or utilize locally sourced ingredients. Some examples of commonly used complex minerals include pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), colemanite ($\text{Ca}_2\text{B}_6\text{O}_8(\text{OH})_6 \cdot 2\text{H}_2\text{O}$), ulexite ($\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 8\text{H}_2\text{O}$), fluor spar (CaF_2), dolomite [$\text{Mg, Ca}(\text{CO}_3)_2$], spodumene ($\text{LiAl}(\text{SiO}_3)_2$), and soda ash (Na_2CO_3). For C-glass fiber, albite ($\text{NaAlSi}_3\text{O}_8$) is commonly used to reduce the need for soda ash. For simplicity, primary phases of the above natural raw materials are used; all of them can contain other mineral phases and/or impurities, for example, iron from ore and grinding process.

Batch reaction chemistry and kinetics in glass melting have been widely studied with various experimental techniques, including differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray diffraction, electrical resistance and temperature distributions from molten glass to the batch pile, for laboratory batch sizes from as little as 0.1 g up to 10 kg in mass [12–14]. Models have also been developed from a thermodynamic approach [15].

As illustrated in Figure 3, the batch-to-melt conversion process of representative E-glass and ECR-glass batches can be characterized in the following steps:

- i) De-hydroxylation of batch ingredients, i.e. removal of both moisture water (120–150 °C) and crystalline

water in the minerals, (colemanite, 350–450 °C; kaolinite or pyrophyllite, 500–600 °C).

- ii) Decarbonization, i.e. removal of carbonates (limestone, 700–800 °C).
- iii) Formation of intermediate crystalline phases (~1000 °C).
- iv) Liquid phase formation (1000–1400 °C).
- v) Final dissolution of residual phases (sand, 1250 °C) [12].

The majority of the batch reactions are endothermic, the energy consumption of these steps constituting a significant portion of the total energy spent in the glass melting process. Finally, the glass fining step, which varies as a function of furnace throughput, consumes even more energy. The fiberglass industry is continuously searching for new raw materials to lower the energy consumption in batch melting [12] and improved technology to increase the furnace throughput without sacrificing glass quality. This in turn reduces the unit energy consumption of glass melted and glass fiber produced. In practical terms, successful implementation of these approaches can provide savings of up to 20% compared to typical E-glass melting energy demands of 7000–8000 kJ/kg of glass [12].

One generally carries out glass melting and fining by controlling the melt temperature of the furnace hot spot near or higher than T_M at which the melt viscosity is 10 Pa·s (Figure 4), which will ensure sufficient fluidity of the molten glass to promote both mixing of the batch components and removal of seeds (or bubbles). The latter is also aided by the use of fining agents such as sodium sulfate (Na_2SO_4), which is commonly used in making E-glass fibers. However, because much higher melting temperatures are often required for specialty glass fibers, other fining agents such as manganese dioxide (MnO_2) or cerium dioxide (CeO_2) are also used with or without

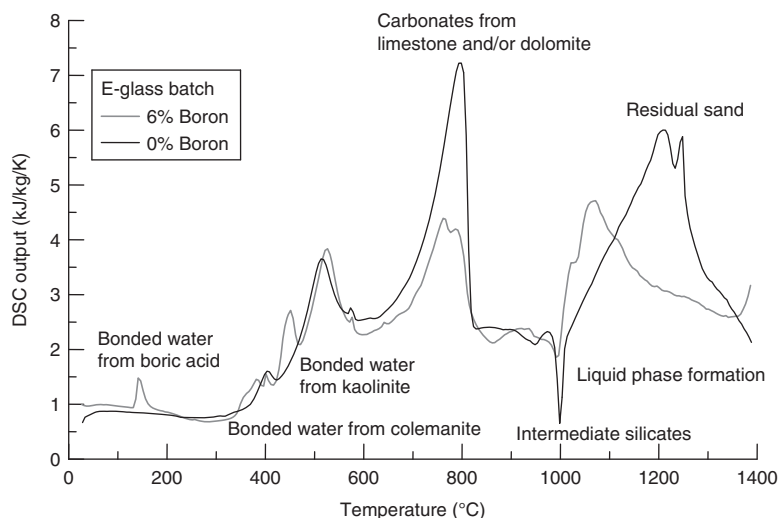
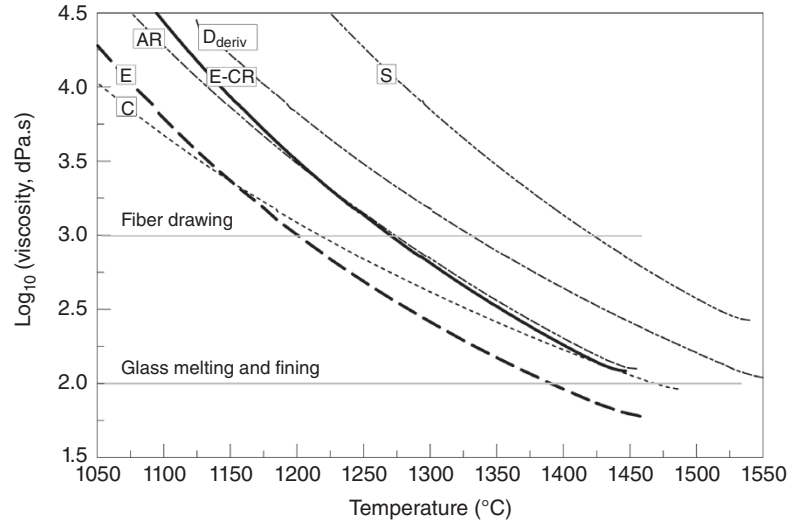


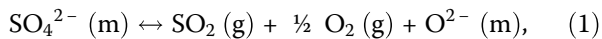
Figure 3 Differential scanning calorimetry output of E-glass batches with and without boron from room temperature to 1400 °C (10 K/min heating rate), illustrating both endothermic and exothermic reaction events as batches are converted into glass through initial steps of dehydration and decarbonation. The intermediate silicates formed are anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and/or wollastonite (CaSiO_3). Source: PPG, 2014.

Figure 4 Viscosity curves of E-glass, E-CR-glass, AR-glass, D-glass (derivate), S-glass, and C-glass, illustrating composition effects on reference temperatures of glass melting/fining and fiber drawing. Source: PPG, 2014.

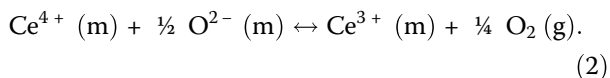


added sodium sulfate. Fining agents may also serve as oxidizing agents to control the iron oxidation states for both glass melting and fiber drawing process as will be discussed in more detail in a later section.

Fining action from the decomposition of Na_2SO_4 dissolved in the melt is created as the molten glass stream moves toward the higher temperature fining zone, or hot spot, of the furnace. The melt with dissolved sulfate becomes oversaturated at higher temperatures ($>1350^\circ\text{C}$) and sulfate decomposition and bubble formation begins to occur. The onset temperature of sulfate decomposition depends on many factors – water vapor pressure in the furnace combustion space, water dissolved in the glass, organic species in the batch materials, any addition of carbon to the batch, partial pressure of oxygen above the melt, and others [16]. Driven by buoyancy action, bubbles containing SO_2 and O_2 travel to the melt surface; along the way the sulfate bubbles expand, stripping smaller bubbles of CO_2 (primarily from decomposition of carbonates) and air (primarily N_2) trapped in the melt. The sulfate fining process can be described by the reaction



where O^{2-} is the free oxygen, which depends on glass composition. With other fining agents, for example CeO_2 , oxygen fining gas is generated according to the reaction



Adequate use of fining agents is critical. The quantity needs to be optimized based on the furnace firing setup, types of fuel and air or oxygen used, glass composition,

and types of fiber products to be made. Excessive use of fining agents can result in uncontrolled melt foaming. The foam layer reduces energy transfer from the combustion space to the glass melt beneath the foam blanket, resulting in energy waste because of excessive firing required to maintain the underglass temperature and in poor glass quality caused by inhomogeneous melting. Excessive foam can also lead to potential overheating of the furnace crown, shortening the furnace service life.

3.3 Fiber Forming

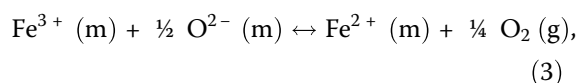
The *bushing* is the device that controls the fiber-drawing process. It is the interface between the glass melting and fiber formation processes. Bushings are made of precious metal alloys of platinum (Pt) and rhodium (Rh), typically in alloys of 90Pt/10Rh or 80Pt/20Rh. The tip plate of the bushing contains an appropriate number of tips or nozzles, typically ranging in number from 100 up to 8000 and in diameter from 0.75 to 2.00 mm. Proper selection of these parameters then enables production of the desired number and diameter of glass fiber filaments in a strand of fiberglass (Figure 2b). The bushing is electrically heated to provide very precise control of the temperature and, thus, of the viscosity of the glass flowing through the nozzle. The combination of tip size and glass viscosity coupled with the controlled speed of the take up winder allows for very good control of finished-product filament diameters and linear-strand density.

The rate of melt flow (F) through the bushing nozzle or bushing tip follows Poiseuille's relationship, i.e. flow is proportional to $r^4 h / l \eta$ where r is the fiber radius, h is the depth of molten glass above the bushing tip plate, l is the length of nozzle, and η is the melt viscosity at the tip plate [3]. In practice, the actual interior geometry of

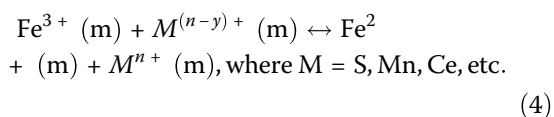
the nozzle may be varied, which affects the melt flow rate for a given winder speed; modified Poiseuille equations can be found in the literature [3].

The fiber attenuation process is usually completed in less than a second, during which the diameter of the melt stream through the tip changes by three orders of magnitude from millimeters at the tip to micrometers in the finished filament. At a fiber attenuation speed between $3 \cdot 10^4$ and $3 \cdot 10^5$ m/s, depending on bushing type and specified fiber product, the estimated fiber cooling rate is approximately $0.5 \cdot 10^6$ K/s for a typical commercial fiber-forming process. Stable drawing processes require adequate control of the fiber cooling rate, which is managed through a combination of process controls, including appropriate bushing design, cooling manifolds (commonly known as fin coolers), cooling air flow, and water spray. In addition, one optimizes the fiber drawing and cooling rates by tuning the oxidation state of iron (either from raw material impurities or intentionally added) in the glass, specifically the concentration of ferrous ion (Fe^{2+}).

The oxidation–reduction of iron in the melt is affected by glass chemistry and oxygen partial pressure ([16, 17], Chapter 5.6)



and by the presence of other multivalent species either from additives or impurities,



In general, drawing processes for making finer or smaller diameter fibers (and typically smaller bushings also) require glasses with a relatively lower concentration of Fe^{2+} (hence, slower cooling rate) than coarse fibers made from larger bushings (hence, higher cooling rate). The control of the iron oxidation state (or ferrous ion concentration in glass) is directly related to the amount of fining agent in the batch and the total iron in the batch, both of which are adjustable variables to maintain process stability. The ferrous ion concentration in glass is routinely monitored in production with a colorimetric method through acid digestion of a glass powder sample or with a calibrated UV-VIS spectroscopic method on an optically polished glass disk.

In commercial production, glass fibers are drawn at a temperature T_F where melt viscosity is near 100 Pa·s (Figure 4). Stable melt viscosity at the tip plate is critical for an efficient fiber-forming process. If melt viscosity at the tip plate is too low (i.e. too high temperature at the tip plate), spreading of the glass melt across multiple tips on the tip plate results in flooding and disruption. If melt

viscosity is too high (i.e. too low temperature at the tip plate), fiber drawing tension increases and the stable forming cone at the tip exit begins to fail, causing fiber breakage [3]. In addition, the actual forming temperature must be greater than the glass liquidus temperature, T_{liq} , by at least 50 °C to reduce the risk of devitrification. Microcrystals formed in colder spots along a primary canal or forehearth (Figure 2a), no matter how small, can lead to significant fiber breakage in the drawing process and hence, adversely impact productivity.

In making commercial glass fiber products for reinforcements, various processes are used to provide the desired end form. Direct draw or single end winding, direct chopped fibers, and numerous downstream secondary processes may be employed. Depending on the product needs, the types of bushings vary in dimension, number of tips, and tip diameters. In addition to the glass and process elements necessary to produce commercial glass fibers, the surface of the fiber must be treated to provide optimum compatibility of the inorganic glass fiber with the organic resins used in the reinforcements industry. This leads naturally into a discussion on the role of sizing chemistry.

3.4 The Role of Sizing/Binder in Glass Fiber Products

The long history of growth in both volume and breadth of glass-fiber commercial successes has been driven by unique combinations of strength, stiffness, weight, and cost attributes that can be achieved through glass chemistry. However, to realize fully the value of the glass fiber in a reinforced composite, a means must be provided to facilitate the effective interactions between the inorganic fiber and the organic polymer that together make up a reinforced composite material. One maximizes this interaction by designing an interface that synergistically combines the material properties of each element. A design that provides for effective load transfer between the constituents transforms an inherently heterogeneous material into one that behaves as a homogeneous structure.

In fiber-glass composites, the system that delivers the optimum interfacial properties is the *sizing* or binder that is applied to the surface of the fiberglass. The sizing is generally applied as a continuous coating just after the fibers are formed and before the individual glass filaments are gathered into a strand below the bushing. The most common sizing formulations comprise a water-based mixture of molecular species such as adhesion promoters, film formers, lubricants, and other processing aids as summarized in Table 4. It is the role of the sizing chemist, working in conjunction with the glass scientists and the process engineers, to deliver a sizing formulation that appropriately enables efficient production rates of the

Table 4 Classification and functionality of ingredients in fiber sizing/binder formulations.

Classification	Functionality
Coupling agents	Adhesion promoters that bond or couple the glass surface with specific matrix resin systems; may also provide excellent filament protection and increased dry breaking strength.
Film formers	Hold filaments together and provide protection to the fiberglass strand.
Film modifiers	Modify the film formation to increase strength, flexibility, and tackiness.
External lubricants	Provide resistance to abrasion damage at external contact points such as strand guides in downstream processes.
Internal lubricants	Reduce the filament-to-filament abrasion within the fiberglass strand.
Emulsifiers/ Surfactants	Form stable suspensions or emulsions of immiscible ingredients, generally in water-based systems.
Other process aids	May be used as required to control foam, wetting, static behavior, biological activity, and any other special requirements by a particular end-use or internal processing need.

fiberglass while also providing maximum compatibility with the targeted composite polymer matrix and the end-use performance requirements.

Good sizing design begins with a selection of the appropriate adhesion promoter that will provide good bonding between the inorganic glass surface and the reactive sites in the targeted polymer system. The most widely used class of chemicals for this function are organosilanes. These species can be designed to promote reaction between the silanol sites on the glass surface and on the organosilane molecule, leading to an Si–O–Si bond at the glass/polymer interface. The silanes as supplied are hydrolyzed in the final sizing formulation to provide Si–OH groups that can then condense with the Si–OH groups on the glass surface to provide strong interfacial bonds. The organic functionality of the silane is then chosen to maximize compatibility with the target polymer in the final composite. Common examples are shown in Table 5. Other classes of chemicals that have seen more limited utility as adhesion promoters include organotitanates and organo-chromium complexes.

It is important to note that characterization of the quality of the sizing as well as the glass fiber in the finished composite is critical to confirming technical success of a fiberglass product. Good adhesion at the interface implies the formation of an interphase that makes the materials compatible through covalent bonding, and provides a discrete pathway for stress transfer between the materials. Many standardized tests related to interfacial adhesion, interfacial shear stress, tensile stress, modulus, and hydrolytic stability have been developed over the years and are widely available in international standard testing organizations such as ASTM and ISO. Many academic laboratories have also developed more sophisticated tests. One example is the measurement of composite critical fiber length [18]. As defined by Eq. (5), the critical fiber length (l_c) is the minimum fiber

length at which fibers with given diameter d reach their ultimate tensile strength σ_{fu} and the matrix/fiber interface experiences a maximum interfacial shear stress τ_y , [18]. When $l > l_c$, an increase in interfacial adhesion will result in a decrease in critical fiber length and may lead to improvements in other properties such as impact strength in certain resin systems. However, the sizing may also act to protect the fiber from surface damage and defects in addition to providing improved adhesion. In that case, reduction of fiber surface damage would lead to an increase in the critical fiber length by increasing σ_{fu} . Interestingly enough when $l > l_c$ and the composite is stressed to failure, then the fiber will break at regular intervals of l_c within the composite. This result can be used to estimate the interfacial shear stress:

$$l_c = \frac{\sigma_{fu}}{2\tau_y} d \quad (5)$$

This example also serves to illustrate that broader conclusions from micromechanical experiments should consider that different outcomes may result depending upon material selection. The most common material options include chopped or short fibers vs. continuous fibers and thermoset vs. thermoplastic resin systems, which of course complicates the task of the sizing chemist in product development.

It remains for the sizing chemist to complete the establishment of the final formulation from a virtually limitless palette of film formers, process aids, and modifiers to deliver the desired performance of the fiberglass as a commercial product. Commercially, the resultant amount of sizing on the fiberglass surface is typically in the range of 0.3–1.5 wt % of the dry fiberglass.

An excellent in-depth review of the complexity of this field from the sizing chemists' point of view can be found in Thomason's book, *Glass Fibre Sizings: A Review of the Scientific Literature* [19].

Table 5 Common organosilanes.

Chemical name	Structure	Class
γ -Aminopropyl trialkoxy silane	$(\text{RO})_3\text{Si}-(\text{CH}_2)_3-\text{NH}_2$	Amine
γ -Methacryloxypropyl trialkoxy silane	$(\text{RO})_3\text{Si}-(\text{CH}_2)_3-\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$	Methacryl
γ -Glycidyloxypropyl trialkoxy silane	$(\text{RO})_3\text{Si}-(\text{CH}_2)_3-\text{O}-\text{CH}_2\text{CHCH}_2\text{O}$	Epoxy
Vinyl trialkoxy silane	$(\text{RO})_3\text{Si}-\text{CH}=\text{CH}_2$	Vinyl
R = CH_3CH_2- or CH_3-		

4 Markets and Applications

4.1 Global Glass Fiber Reinforced Polymeric Composite Markets

The glass fiber reinforced polymeric composites market will grow from about \$18 000 million in 2010 to an estimated \$30 000 million in annual shipment value by 2017 according to a recent survey. These composites find many applications in commercial markets globally. A breakdown by major regions of the world is shown in Figure 5 for the Americas, EMEA (Europe, Middle East, and Africa), and Asia Pacific.

Construction and transportation dominate the Americas market place for GRP composites, with construction taking the largest share. Other segments are more or less equally distributed among industrial, oil and gas, and wind-turbine blade applications, along with numerous smaller segments. In the EMEA region, construction and transportation are also the largest markets, but here the leading industry is transportation. The wind-turbine blade segment is much higher in Europe, and the other segments hold similar shares as seen in America. In the Asia Pacific region, once again transportation and construction combined are the largest segments. In this region, however, electronics and industrial markets are more prominent, combined with a large “other” segment driven by the large variety of needs and applications in the region. The electronic segment is particularly strong, reflecting the strong position of the PWB industry and its supply chain of E-glass fiber, fabric, and laminators in the Asia Pacific region.

Generally, GRP composite materials are classified into two categories: thermoplastic and thermoset. Thermoplastic GRP products most commonly use resins based on polypropylene, polyamides (nylon 6 and 6,6), polyesters (polybutylene terephthalate, polyethylene terephthalate), and many other specialized thermoplastic polymers. Thermoset GRP products commonly use resins based on epoxies, unsaturated polyesters, and vinyl esters, with smaller but growing applications use phenolic and urethane-based resin systems as well as other

specialty resins. Thermoplastic resins generally exhibit higher ductility and impact resistance, while thermoset resins offer better strength and modulus and higher thermal stability. There are many new developments underway in both processing and resin chemistry that often blur the traditional divisions between thermoplastic and thermoset-based glass fiber composites. The glass fiber industry will continue to be at the forefront in supplying reinforcement solutions for these new developments.

Thermoplastic automotive applications include window frames, automobile body components, dashboard sections, and bumper beams. Typical processes for combining fiber forms with thermoplastics resins as intermediates for molding of final parts include extrusion compounding of short fibers, glass-mat thermoplastic sheet, and long-fiber thermoplastic compounding.

Major thermoset products include composite pipes for oil and gas, marine, and industrial applications; wind-turbine blades; flue-gas desulfurization tanks and towers; PWB; boats; construction beams and structures; composite leaf springs; and numerous sporting-goods applications. Other components are countless and limited only by the imagination. Typical conversion processes for thermoset composites include filament winding, pultrusion, resin transfer molding, hand lay-up, spray deposition, continuous laminating, centrifugal molding, sheet molding compounds, and bulk molding compounds.

Glass fibers can also be used as a reinforcement for cement structures, in many cases with AR-glass fibers as already noted. Like E-glass, it also finds utility in some of these applications where short-term strength is the major requirement. Some geotextile reinforcements also use E-glass as a base in a coarse mesh form. Chopped glass fibers are the predominant reinforcement for asphalt roofing shingles, primarily in North American markets (*Source: fiber glass market study, PPG, 2014*).

4.2 Emerging GRP Composite Markets

Traditional E-glass still dominates total glass fiber volume produced around the world, with a well-established

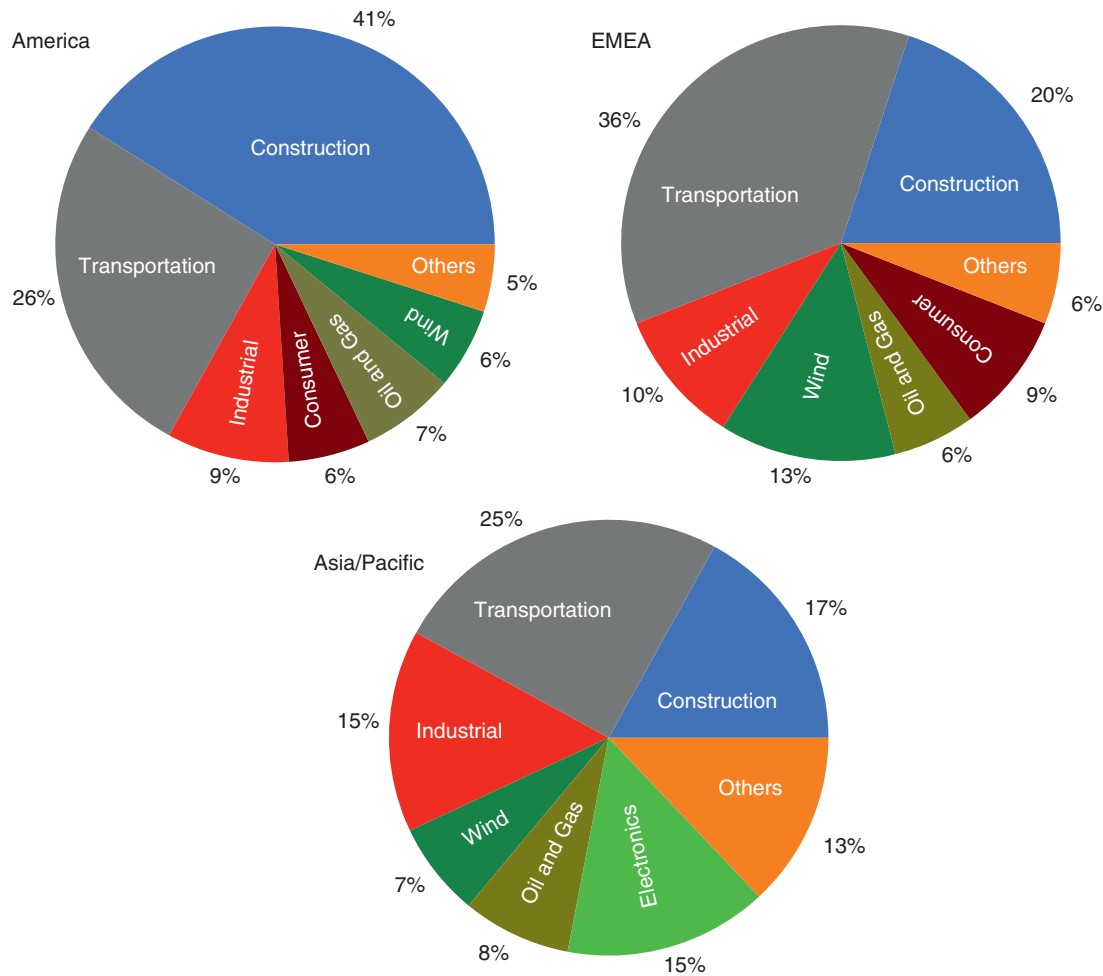


Figure 5 Global GRP composite market shares in America, EMEA, and Asia Pacific regions. Source: Fiber glass market study, PPG, 2014.

history of delivering value in many markets for more than 70 years. This trend is expected to continue because of the E-glass value in use and the maturity of the manufacturing technology. Along with its variants, E-glass will continue to be the material of choice in most applications. Fiber manufacturers will continue to move toward more environmentally compliant variants, and product development scientists will continue to tailor the glass composition, form factor, and surface chemistry to maximize synergy with developing resin chemistries and process technologies. A good example of this evolution is E-CR glass and its performance in strongly acidic environments. This adequacy has resulted in the specification of E-CR glass as a requirement in applications such as waste water pipe systems, desulfurization towers in power plants, and filtration bags in power plant or cement productions (Figure 6a).

Specialized fibers, including redesigned and more manufacturing friendly versions of S-glass, R-glass,

and D-glass for high-strength, high-modulus, and premium electrical properties, respectively, continue to be in demand where limits are being pushed to the extreme for traditional E-glass. Some examples include aerospace, driven by weight and fuel economies; wind energy, driven by the need for increased stiffness at a fair value cost in order to achieve lower energy costs; transportation, driven by fuel economy and energy management in crashes; better electrical properties, driven by increased bandwidth, faster computing speeds, and miniaturization; and energy storage, driven by higher strength for hydrogen storage tanks and other components. A specific example of the role of improved glass design is related to the design of ultra-long wind-turbine blade. Newly designed high modulus and low-density glass fibers will likely replace E-glass fibers (Figure 6b) in the future, helping to drive the unit cost of electricity generation to a more competitive level.

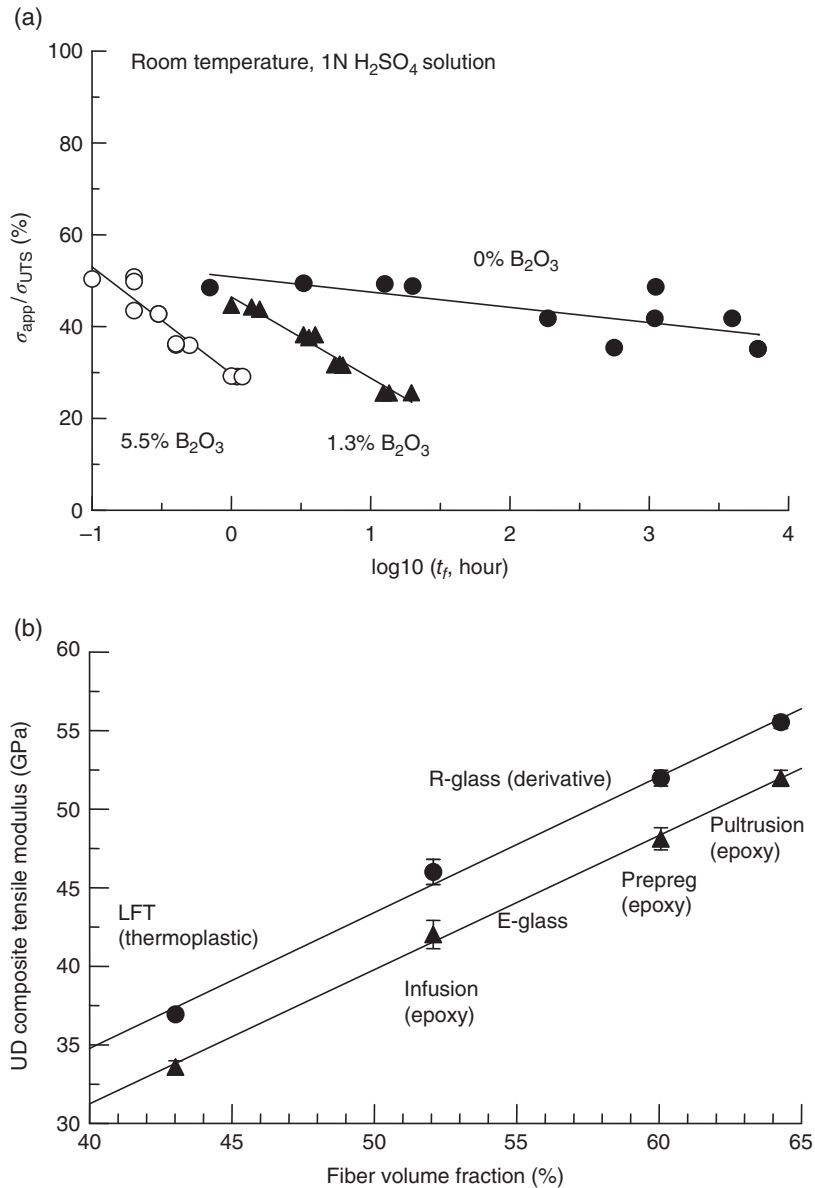


Figure 6 Improvement in fiber properties through compositional changes. (a) Effects of boron reduction on acid stress corrosion performance as shown by a comparison of boron-free ECR and E-glass fibers [7]. (b) Improvement of composite unidirectional tensile modulus with newly designed R-glass fibers for various potential applications for both thermoplastic and thermoset composites [4] (σ_{app} – applied tensile stress on rod samples, σ_{UTS} – ultimate tensile strength of as-received rod samples, unidirectional nonwoven fabric reinforcement – UD composite panel, long fiber thermoplastics – LFT).

5 Perspectives

It is expected that E-glass and its variants will continue to be the predominant form of glass fiber for most reinforcements markets in the near term. However, as larger volume applications grow with increased performance needs, the glass fiber industry will face challenges to develop manufacturing technology platforms capable of making these products at costs acceptable to the markets. Innovation is needed in both glass chemistry and manufacturing technology to grow specialty fiber businesses that usually provide higher profitability than traditional glass fiber

markets. Some examples of manufacturing technologies could include new melting furnace designs, new melting techniques, new fining methods for higher temperatures, and new refractory materials for high-temperature operations. In terms of fiber-glass chemistry, an in-depth fundamental understanding of glass structure–property relationships will aid glass optimization for performance and manufacturing scalability. Most ongoing research, including molecular dynamic modeling, focuses on local structure of both network work formers (primarily Si, B, and conditionally Al) and network modifiers (primarily alkali, alkaline earth, and rare earth).

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1.7

Simulation in Glass Processes

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1 Introduction

Numerical simulations of glass processes are performed in lieu of physical trials, which often involve conditions too harsh to allow measurements, are difficult to control, or are prohibitively expensive. Used as a screening tool, a simulation model can thus allow technologists to avoid several iterations of actual physical trials on an industrial apparatus. Alternatively, simulations can be used to examine phenomena which are too difficult to observe in practice because of the extreme environment of glassmaking. Moreover, numerical simulation allows for fundamental phenomena to be studied, thanks to its capability of identifying and controlling factors that influence the process. Such factors cannot usually be independently modified in the real process, in view of its complexity, and the insights gained from such virtual experiments can be used to guide technology development efforts.

Following the advent of electronic computers in the mid-twentieth century, these methods were pioneered in the 1960s to deal with glassmaking problems elementary enough to be handled with the simplifying assumptions required by the then limited computing power. Much more complex and realistic 3-D problems can of course be tackled now as massive increase in this computing power has dramatically changed engineering analysis in general. Concomitant with hardware advances have been significant developments in software, including both computational algorithms and user interfaces. Several commercial offerings of the relevant software are available for glassmaking. Process engineers are encouraged to utilize such tools. Some of these software packages are general purpose, adaptable to a wide range of situations,

whereas others serve the glass-processing industry specifically.

Both general-purpose and niche-software products will be used in the example simulations presented in this chapter where the focus will be put on the mathematical techniques used to simulate the two major phenomena involved in glassmaking, namely fluid flow and heat transfer. Mathematical models, formulated from the classical laws of physics, are used to calculate relevant field variables, such as temperature, velocity, stress, etc., within a glass manufacturing process. Modeling results are then interpreted with post-processing procedures, which are less abstract than ever before, thanks to modern techniques capable of displaying results in a geometrical context. When applied to fluid flow and heat transfer, these techniques are collectively referred to as *computational fluid dynamics* (CFD).

To review these new methods, we will first summarize the main six steps they successively involve from the definition of the problem of interest to its solution. The various physical phenomena relevant and their mathematical description and computational treatment will then be expounded. Subsequently, a few representative examples of model simulation will be presented to demonstrate the capabilities and the value of modeling to a glass manufacturing enterprise. Finally, a brief section on the importance of managing simulation data will be provided.

2 A Brief Overview

Numerical simulation is a process made up of the six steps summarized in Table 1. These are: (1) identify the objectives of the modeling study, (2) construct a geometrical domain and discretization of the system of interest (i.e. meshing or grid generation), (3) build the simulation

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Table 1 Summary of simulation process steps.

Step	Process	Description
1	Objective	Identify needed results – quantitative summaries – qualitative insights – comparisons.
2	Geometry and mesh	Construct CAD model and discretize into elements or cells.
3	Physical conditions	Assign materials and properties to regions, boundary conditions, sources, and other abstractions to account for physical behavior. (Can affect Step 2)
4	Solve	Select solver options, such as under-relaxation coefficients, gradient estimation methods, convergence criteria, etc., and solve. (Can affect Step 2 or 3)
5	Post-process	Review computed results, prepare contour plots, vector plots, flow pathlines, and other computed values from results.
6	Document and archive	Prepare presentation or report and store all information in appropriate database.

model by selecting physical phenomena and applying various physical data (e.g. material properties, boundary conditions), (4) choose numerical parameters to execute the calculations and effect a solution, (5) post-process the simulation results, and (6) document them and archive the modeling data. Each of these is important, and some are mutually dependent on one another.

The first step of identifying the objective cannot be overemphasized. It will drive the rest of the process and will lead to key assumptions to be applied along the way. The complexity of the model or its level of detail can very much depend on its purpose. Thus, the second step of geometrically defining the computational domain and discretizing it very much relies on the modeling objectives and requires good judgment in order to resolve the details of interest without adding human and computational effort that are not key to the objectives sought. Therefore, it is crucial to determine a good balance between model accuracy and the effort needed to reach a solution.

Generating a mesh is often the main bottleneck in the modeling process, as it is often rendered difficult by geometrical details which have a negligible effect on the results of interest. Meshing software with de-featuring options may be helpful, but good guidance at the outset of the modeling project is very valuable. This point is well illustrated in Figure 1a where are sketched two ways to represent a burner block used in a hearth (i.e. the heated canal lined with refractory material separating the melting furnace from the forming machinery). The geometry shown in Figure 1a more accurately represents the actual shape of the burner block, but it yields highly skewed and undesirable mesh cells. The low-quality mesh is the result of three surfaces, one of which is curved, intersecting at a point, which will either cause divergence of the computational algorithm or lead to spurious results. Extreme grid refinement thus is required to achieve acceptable mesh quality. An alternative that alleviates the meshing problem, without having a significant effect on computed results, is shown in Figure 1b.

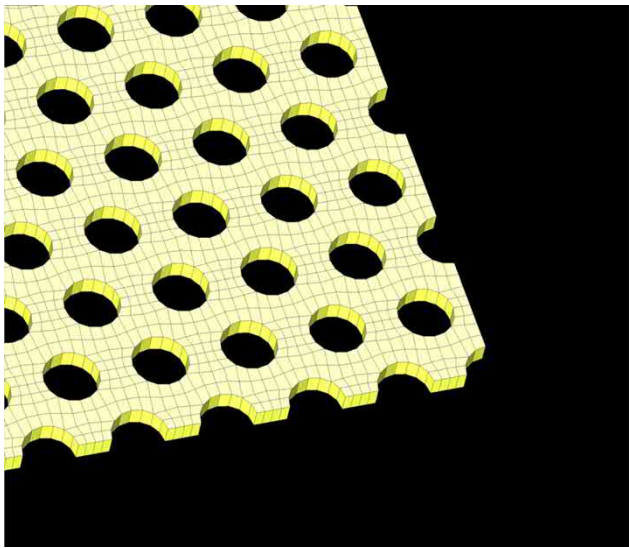
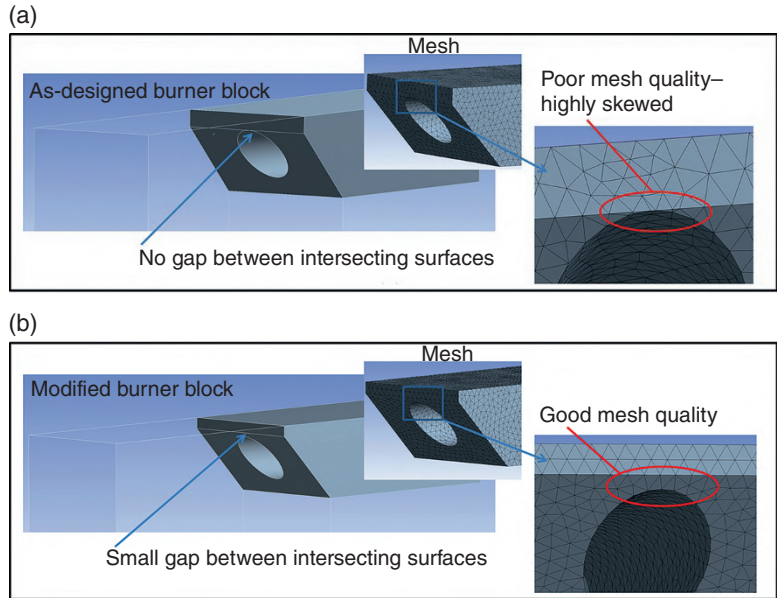
Sound engineering judgment is also needed to build the simulation model, the third step of the simulation process. Many decisions are required. For example, can symmetry be assumed? Another example is linked to the steadiness of the process and whether an assumption of steady state is justified or if transient conditions must be considered. Treating fundamental properties like viscosity (Chapter 4.1) and thermal conductivity (Chapter 4.5) as constant or temperature-dependent represents another decision that must be made by the numerical analyst. Sometimes, it is advantageous to use constant properties to establish an initial solution, followed by another solution attempt with variable properties. This strategy has been used effectively where the initial constant property solution serves as the initial estimate for the more accurate, variable property simulation. It is recommended to begin a simulation project erring on the side of simplicity, and then to add complexity in subsequent simulations.

It is also the case that the physical modeling decisions will affect the geometrical and meshing procedures. For example, a perforated plate through which a fluid flows could require extremely detailed meshing (Figure 2); or the effects of the hole pattern could be accounted for with a much less refined mesh using a more abstract method, in which the screen is characterized by a permeability which relates velocity and pressure drop. The decision on how to proceed will depend on the objectives of the study.

Post-processing (Step 5) is also very important, as it requires the analyst to execute good judgment on the results obtained. Before extracting information and insights from the results, the analyst must scrutinize the calculated field variables, as well as checking for balanced conservation laws; that is, checking for sufficient numerical convergence must be performed. Finally, management of simulation data (i.e. electronic model files) should not be overlooked since it determines the efficiency with which the simulation process is executed.

Figure 1 Examples of burner block geometry.

(a) Accurate representation with poor mesh quality;
 (b) slight modification with improved mesh quality.

**Figure 2** Example of a screen with small-scale features requiring a high mesh density to be resolved.

3 Fundamental Phenomena, Governing Equations, and Simulation Tools

3.1 Glass as a Continuum

The basic principles of engineering science are applied in CFD simulations. These involve fluid mechanics and usually various other phenomena that are typically considered to fall within the category of thermal sciences. A brief overview is provided, but for complete development, interested readers not yet familiar with the details are referred to various textbooks (e.g. [1–3]). Physical

phenomena specific to glass processes must be accounted for within the framework of three fundamental principles and will be reviewed later with respect to a few chosen examples. Readers are also directed to a volume edited by Krause and Loch [4] for a collection of excellent examples of numerical simulations applied to glass processes.

Forming the foundation on which CFD models are constructed, the fundamental principles of classical physics account for conservation of mass, momentum, and energy. Conservation of momentum follows from Newton's three laws of motion, whereas energy conservation is of course the first law of thermodynamics. Contrary to what is done for the very small systems simulated in theoretical studies (Chapters 2.8 and 2.9), it is impractical to account for the motion or energy level of each individual atom or structural entity at the scale relevant to industrial processes. Instead, it is recognized that, for length scales of engineering practicality, substances can be characterized with intensive properties (i.e. per unit volume or mass). Because it describes the mass per unit volume of a particular substance, density is a simple example of such a property that is independent of the size of the system. This abstraction allows substances to be treated as a *continuum* and allows for powerful mathematical models to be constructed.

3.2 Transport by Advection and Diffusion

Referring again to well-recognized texts [1, 2], we will remind that the principle of conservation of mass, applied to an infinitesimally small control volume (CV), is mathematically expressed as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = 0, \quad (1)$$

where ρ is the density and $\vec{V}$ is the velocity vector. Equation (1) is often called the continuity equation. A mathematical expression of the conservation of momentum is

$$\frac{\partial (\rho \vec{V})}{\partial t} + \nabla \cdot (\rho \vec{V} \vec{V}) = \nabla \cdot (\vec{\sigma}) + \vec{B}, \quad (2)$$

whose left-hand side represents the time rate of change of momentum (i.e. mass times acceleration), and the right the forces acting upon the fluid by adjacent fluid particles (i.e. the divergence of the stress tensor, $\vec{\sigma}$) and other relevant objects through gravity or electromagnetically generated forces (i.e. a net body force per unit volume, $\vec{B}$). Forces attributable to adjacent fluid particles are collectively represented by *stress*, which is another intensive property quantifying force per unit area.

An important requirement for mathematical modeling of fluid flows is to relate internal fluid stresses to characteristics of the fluid's motion. Such a relationship, which depends on the substance, is termed a *constitutive relationship*. There are many types of material behavior, requiring different constitutive models, but the most commonly used model relates shear stresses to strain rate (i.e. velocity gradient) in a linear manner. Fluids to which this linear relationship applies are known as Newtonian fluids. For example, a shear stress component τ_{xy} for a Newtonian fluid is characterized with

$$\tau_{xy} = \mu \frac{\partial u}{\partial y}, \quad (3)$$

where μ is the dynamic viscosity and u is the x -direction component of the velocity vector. For a Newtonian fluid, viscosity is independent of the strain rate. As long as it is homogeneous, glass is a Newtonian fluid although its viscosity is a very strong function of both composition and temperature (Chapter 4.1).

When the Newtonian constitutive model is substituted into the more general momentum Eq. (2) and the fluid is assumed to be incompressible, the result is the well-known Navier–Stokes equation

$$\frac{\partial (\rho \vec{V})}{\partial t} + \nabla \cdot (\rho \vec{V} \vec{V}) = \nabla \cdot (\mu \nabla \vec{V}) - \nabla P + \vec{B}, \quad (4)$$

where P is the fluid pressure. Not all fluids behave according to Eq. (3). Such non-Newtonian fluids must be mathematically modeled with different constitutive relations substituted into Eq. (2) [5, 6].

Note that Eq. (4) is a vector equation, although it can be decomposed into vector component (scalar) equations, which is often done for the numerical application. In

Cartesian coordinates, these component (scalar) equations are the following:

$$\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho \vec{V} u) = \nabla \cdot (\mu \nabla u) - \frac{\partial P}{\partial x} + B_x, \quad (5)$$

$$\frac{\partial (\rho v)}{\partial t} + \nabla \cdot (\rho \vec{V} v) = \nabla \cdot (\mu \nabla v) - \frac{\partial P}{\partial y} + B_y, \quad (6)$$

$$\frac{\partial (\rho w)}{\partial t} + \nabla \cdot (\rho \vec{V} w) = \nabla \cdot (\mu \nabla w) - \frac{\partial P}{\partial z} + B_z. \quad (7)$$

In fluid mechanics problems, the unknown field variables are the three components of velocity (e.g. u , v , and w) and fluid pressure, requiring four independent equations, which are the three momentum component Eqs. (5)–(7) and the continuity Eq. (1).

The equation for energy conservation is derived in a similar fashion. A common form of the energy equation is

$$\frac{\partial (\rho C_p T)}{\partial t} + \nabla \cdot (\rho C_p \vec{V} T) = \nabla \cdot (k_t \nabla T) + S_T, \quad (8)$$

where C_p and T are the specific heat and temperature, respectively, and k_t the thermal conductivity. In Eq. (8), the transient and advective transport terms are on the left side, whereas the right side has the conduction term and all other energy transfers accounted for as “sources.” An example of a “source” is Joule dissipation; that is, electrical energy converted to thermal energy by an electrical current passing through a resistive material (with an associated drop in electric potential).

In CFD, various transport phenomena are cast in the following general form known as the advection–diffusion equation [7],

$$\frac{\partial (\rho \phi)}{\partial t} + \nabla \cdot (\rho \vec{V} \phi) = \nabla \cdot (\Gamma \nabla \phi) + S_\phi, \quad (9)$$

where ϕ represents a generic field variable related to the property of interest, and Γ a generic diffusion coefficient. For example, temperature is the relevant field variable in the energy Eq. (8). (Likewise, ρC_p is substituted for ρ in the energy equation as it represents its “thermal inertia” per unit volume.) The first member on the left side of Eq. (9) is a transient term, which can be ignored for steady-state problems. The second is the advection term, representing transport by fluid motion. The first member on the right side of Eq. (9) is the diffusion term, representing transport by atomic-scale interactions, and all others are treated as “sources,” often because the model contains mathematical expressions which do not admit to the form of the one of the three standard terms.

Several commonly used mathematical expressions for the advective–diffusive transport of various field variables

Table 2 List of commonly used transport equations in advection–diffusion form.

		ϕ	Transient	+	Advection	=	Diffusion	+	Source
A	Continuity	1	$\frac{\partial \rho}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V}\right)$	=		+	0
B	Momentum (x -direction)	u	$\frac{\partial(\rho u)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} u\right)$	=	$\nabla \cdot (\mu \nabla u)$	+	$-\frac{\partial P}{\partial x} + B_x$
	Momentum (y -direction)	v	$\frac{\partial(\rho v)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} v\right)$	=	$\nabla \cdot (\mu \nabla v)$	+	$-\frac{\partial P}{\partial y} + B_y$
	Momentum (z -direction)	w	$\frac{\partial(\rho w)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} w\right)$	=	$\nabla \cdot (\mu \nabla w)$	+	$-\frac{\partial P}{\partial z} + B_z$
C	Energy	T	$\frac{\partial(\rho C_p T)}{\partial t}$	+	$\nabla \cdot \left(\rho C_p \vec{V} T\right)$	=	$\nabla \cdot (k \nabla T)$	+	S_T
D	Turbulent kinetic energy	k	$\frac{\partial(\rho k)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} k\right)$	=	$\nabla \cdot (\mu_{t,k} \nabla k)$	+	S_k
E	Turbulence dissipation	ε	$\frac{\partial(\rho \varepsilon)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} \varepsilon\right)$	=	$\nabla \cdot (\mu_{t,\varepsilon} \nabla \varepsilon)$	+	S_ε
F	Electric charge/potential	E		+	0	=	$\nabla \cdot (k_e \nabla E)$	+	0
G	Species A	mf_A	$\frac{\partial(\rho mf_A)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} mf_A\right)$	=	$\nabla \cdot (D \nabla mf_A)$	+	S_A

are listed in Table 2. Some are expressions of a fundamental principle, while others are consequences of further abstraction (e.g. turbulent kinetic energy), although still derived from first principles.

In Table 2, the rows D and E show the components of turbulence quantities for turbulent kinetic energy, k , and turbulence dissipation rate, ε . Glass flows are never turbulent, thanks to the stabilizing influence of glass extreme viscosity, in contrast to flows of air, gas, oxygen, combustion fumes, and other fluids that are part of glass processes.

3.3 Turbulence

Turbulence represents an unstable flow condition that is naturally unsteady. Nevertheless, turbulent flows are commonly treated as steady because the velocity field can be well described with time-averaged values, and similarly for other field variables such as temperature. That is, for any given location, a field variable can be decomposed into a time-invariant average, plus a fluctuating component. The time and length scales associated with turbulent fluctuations are small compared with the important features of a glass process, but the effects of these fluctuating quantities are profound and must accounted for in simulation models.

There are many model formulations to account for turbulence, most having variations tuned for specific flow conditions. It is beyond the scope of this chapter to review even a few of them. The so-called k – ε model is the most

prolific, which is why its two equations are mentioned in Table 2. The source terms S_k and S_ε are related to the rate of strain of the average flow.

$$S_k = \mu_t S^2 - \rho \varepsilon \quad (10)$$

and

$$S_\varepsilon = C_{1,\varepsilon} \mu_t \frac{\varepsilon}{k} S^2 - C_{2,\varepsilon} \rho \frac{\varepsilon^2}{k}, \quad (11)$$

where $C_{1,\varepsilon}$ and $C_{2,\varepsilon}$ are model constants, and S represents the modulus of the strain rate tensor determined from the time-averaged velocity field. (The rate of strain tensor is defined as $\dot{E} = \frac{1}{2} \left[\nabla \vec{V} + (\nabla \vec{V})^T \right]$.) Sometimes, these

sources are embellished with additional terms to account for effects such as buoyancy or compressibility.

The purpose of a turbulence model is to account for transport occurring through the turbulent eddies that are not explicitly resolved in the simulation. Such transport occurs through advection as represented by the second term on the left side of the generic transport Eq. (9), averaged over time for steady-state problems. As mentioned above, these eddies are smaller than typical features of interest, but they are much larger than the molecular scale associated with diffusion through the first term on the right side of Eq. (9). The k – ε model accounts for turbulent transport by treating it as a diffusive phenomenon characterized by a “turbulent viscosity,” μ_t ,

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon}, \quad (12)$$

where C_μ is another model constant, which adds up to the Newtonian viscosity to yield an effective viscosity, μ_{eff}

$$\mu_{\text{eff}} = \mu + \mu_t. \quad (13)$$

It is usually the case that $\mu_t \gg \mu$ and $\mu_{\text{eff}} \approx \mu_t$. Likewise, similar substitutions are made for the diffusion coefficients of other transport equations.

3.4 Radiative Heat Transfer

Heat transfer by conduction and convection is accounted for by Eq. (8) (or C in Table 2), which is also compatible with radiative heat transfer applied as a boundary condition on an opaque surface. However, glass and other media (e.g. combustion gases) are commonly semitransparent in glass processes, that is, they emit, absorb, and scatter IR radiation volumetrically.

Radiative heat transfer significantly differs from transport by advection and diffusion so that it cannot be mathematically described by an equation of the form of Eq. (9). It is instead governed by an integrodifferential equation, known as the radiative transfer equation (RTE) [3],

$$\begin{aligned} \frac{dI(\vec{r}, \vec{s})}{ds} + (\alpha + \alpha_s)I(\vec{r}, \vec{s}) &= \frac{\alpha n^2}{\pi} \sigma T^4 \\ + \frac{\alpha_s}{4\pi} \int_0^{4\pi} I(\vec{r}, \vec{s}') \Phi(\vec{s}, \vec{s}') d\Omega, \end{aligned} \quad (14)$$

where $I(\vec{r}, \vec{s})$ represents the radiation intensity at a position $\vec{r}$ and in the beam direction $\vec{s}$; α and α_s are absorption and scattering coefficients, respectively; n is the index of refraction; $\Phi(\vec{s}, \vec{s}')$ the scattering phase function quantifying the portion of incident radiation from any direction $\vec{s}'$ redirected into direction $\vec{s}$; and $d\Omega$ is a differential solid angle. The absorption coefficient and index of refraction are material properties, whereas the scattering coefficient and phase function Φ depend on physical conditions (e.g. size of soot particles), as well as on material characteristics. Note that Eq. (14) reduces to a first-order differential equation when scattering is not considered.

As for the first term on the left side of Eq. (14), it represents the change in beam intensity per unit length in beam direction $\vec{s}$, whereas the second accounts for the decrease in beam intensity caused by the combined actions of absorption and scattering. While absorption has the effect of increasing local temperature, scattering only redirects a portion of the beam without absorbing energy. Finally, on the right side of Eq. (14), the first term accounts for emission, which tends to lower local

temperatures, and the last term for scattering of IR from all directions into the beam path $\vec{s}$.

Radiation is a directional phenomenon and is in addition spectral in nature in that its intensity in principle depends on the wavelength of the IR beam. When spectral variations can be assumed to have negligible effects, Eq. (14) is written for a medium that is said to be *gray*. Extending the RTE to include spectral effects is straightforward [3], but not presented here.

Note that, Eq. (14) only accounts for IR intensity without determining directly temperatures within a material. Integrated over all directions, however, the net effects of absorption and emission are added to the source term S_T in the energy Eq. (8), thereby affecting local temperatures. There are several methods to account for the directional nature of the RTE. Referring to texts on radiation heat transfer for the details of their derivation [3], we will discuss some of them in Section 4.

3.5 Discretization Methods, Solution Algorithms, and Model Specifications

3.5.1 Finite Element and Control Volume Formulations

Several kinds of computational algorithms exist to solve for the field variable in Eq. (9). One category is known as the finite element method (FEM), where the field variable is assumed to have a functional form or shape over discrete portions of the problem domain. In finite element, the governing equations are multiplied by a weight function and then integrated over an element. The weight function can have various forms. As an example, with the Galerkin method, the weight function is the shape function itself. Another category is known as the CV method, where the problem domain is divided instead into a multitude of small volume elements, each characterized by a single, representative value for each relevant field variable. The conservation laws and fluxes are enforced on each CV, where transport or exchange across adjoining boundaries are determined with finite-difference estimates (usually, a truncated Taylor Series expansion based on unknown or estimated adjacent CV values) of the various derivatives in the governing equation. Whereas both of these numerical methods involve discretizing the problem domain into a multitude of elements or volumes that appear to be virtually the same, they are different as explained in detail in [7, 8]. Generally, more mathematics are involved with the FEM whereas the CV method, dealing with fluxes, can easily be associated with representations giving a physical significance to the problem.

3.5.2 Physical and Numerical Specifications

Once geometrical definition and meshing are done, simulation models are set up with various input

specifications (i.e. Steps 3 and 4 in Table 1). Those associated with Step 3 are physical; that is, they describe the physical characteristics of the process, which in turn affect the degree to which field variables at neighboring grid cells (or mesh nodes) influence each other. Essential are material specifications and associated properties, such as viscosity (for fluids), thermal conductivity, density, specific heat, etc. Many software products have material properties defined for commonly used materials, which must be complemented for materials of interest not dealt with in the existing material database. Various boundary conditions such as flow rates, temperatures, and other state parameters at all flow inlets are other physical specifications to be included along with wall boundaries conditions, which could be, for example, a prescribed temperature, heat flux, or temperature-dependent heat flux.

Every portion of the boundary of the simulation domain requires a boundary condition for each transport equation considered. These conditions can be in the form of a prescribed field variable (e.g. temperature T), prescribed flux by definition proportional to the gradient of the field variable (e.g. $q'' = -k_t \frac{\partial T}{\partial n}$), or a mixed condition where the flux depends on the field variable (e.g. $q'' = h(T - T_c)$). Software products generally provide default values for many of these but, for best practice, much care is recommended to review and verify each boundary condition specification with a checklist. Experience has shown that unintended specifications can be the root cause of the frustrating experience of trying to resolve inconsistencies between simulation results and measured data and/or expectations.

In Table 1, model set up specifications for Step 4 are related to the numerical methodologies employed to render a solution. Examples include so-called under-relaxation coefficients (URCs), which are used to stabilize the evolution of iterative calculation procedures required to solve nonlinear problems. These coefficients are very important since many factors cause virtually all glass-process simulations to be nonlinear.

URCs have values between 0 and 1, where 1 represents no under-relaxation and 0 does not allow the estimated field variable to change from one iteration to the next. In general, larger URC values thus allow for more rapid convergence, but divergence will occur instead if a URC is too high. Conversely, small values of URCs tend to be more robust but require many more iterations to satisfy convergence criteria. It remains a bit of an art to specify URCs, especially because optimal values can very much depend on other numerical specifications.

Additional specifications can include the manner in which advection terms are discretized, whether velocity components are solved consecutively as scalar

components or coupled to one another, along with pressure, or if energy and radiation equations are solved in a coupled or uncoupled manner. Choosing these options can depend on the capabilities of the computer used as algorithms that couple equations require larger amounts of memory.

As just noted, prescribing numerical parameters is an art so that experience is required for an analyst to become efficient and develop realistic expectations. Nevertheless, many commercial software providers offer recommended or default values to begin a simulation. Most numerical parameters will not affect the converged solution, but only the time required to obtain the solution. However, some numerical schemes will provide more accurate results for a given mesh than others although their differences should become imperceptible with sufficient grid refinement. For example, a second-order upwind differencing scheme for advection terms will produce less “false diffusion” than a first-order upwind scheme [7].

4 Simulations in Glass Manufacturing Processes: A Few Examples

4.1 Fundamental Studies

As already stated, the importance of a particular phenomenon can be explored by numerical simulations in such a way that the mathematical treatment and/or its numerical implementation can be examined to assess the best way to account for the physical effects of interest. A good example of this approach was the early one-dimensional study of Glicksman [9] of various physical effects on fiber formation. He formulated his model by manipulating the conservation equations (A)–(C) in Table 2, where glass velocity, filament diameter, and temperature were assumed to vary only in the axial direction of the fiber draw. This relatively simple model was very helpful in understanding the relative roles of glass viscosity and surface tension on fiber-forming dynamics, as well as the influences of radiative and convective cooling.

As computational resources grew, more sophisticated models were developed to explore further fiber-forming dynamics from 2-D axisymmetric models with free surface boundary conditions [10, 11]. Both steady-state and transient simulations were performed and revealed the onset of unstable forming conditions, which could lead to poor product quality and/or reduced process efficiency. A view of the deformed finite element mesh, representing fiber attenuation as it is drawn, is shown in Figure 3, whereas the excellent agreement found between numerical and experimental results of the fiber attenuation (Figure 4) illustrated the reliability of the method.

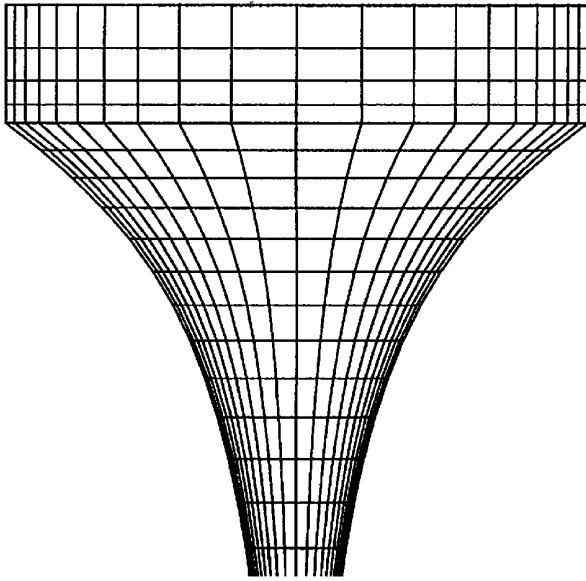


Figure 3 Deformed finite element mesh during a simulation of the drawing of a glass fiber. Source: *International Congress on Glass* [10].

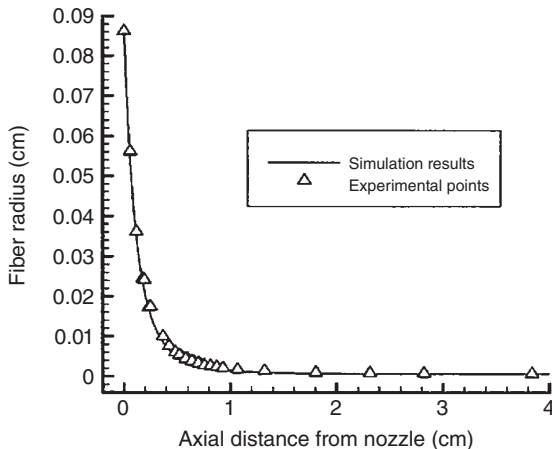


Figure 4 Fiber radius attenuation: comparison of numerical and experimental results for an extension ratio of 19 000. Source: *International Congress on Glass* [10].

Another study examined the manner in which radiation within a semitransparent glass is considered [12, 13]. It was performed in the context of a simplified glass furnace geometry. Because radiative energy is both absorbed and emitted volumetrically, this study examined two methods for accounting the radiative transport with equations (A)–(C) in Table 2. One method is the computationally convenient Rosseland approximation [3], in which one accounts for radiative transport by appropriately adjusting the thermal conductivity of glass; the other employs

the discrete ordinates method (DOM) [3] to solve independently the radiative-transport Eq. (14), the results of which are then coupled to the energy Eq. (8) through source terms. The DOM requires significantly more computational effort and, thus, longer run times. For large models with millions of mesh cells/elements, the difference in run times can be significantly important. For many problems in glass processing, the Rosseland approximation will yield sufficiently accurate results but some situations require a more detailed accounting of the radiative transport. For example, if the refractory-wall temperatures are of interest to assess wear rates, then a DOM might be a better choice. Also, in forming operations, length scales associated with the forming apparatus may be significantly smaller than those for which the Rosseland approximation is valid. A modeling simulation aimed at assessing such fundamental matters is sometimes an appropriate ancillary simulation to perform. Both methods were investigated and compared in [12].

4.2 Glass Melting Furnace

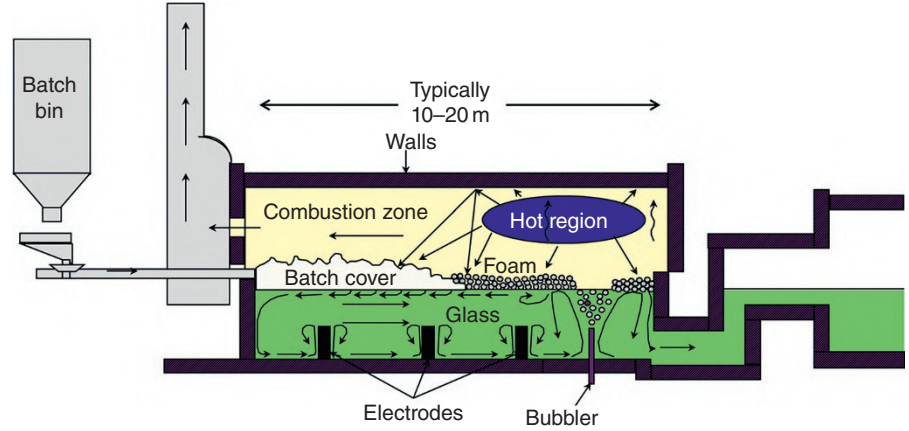
4.2.1 Models

Relatively small simulation models provide a means to understand the behavior of an isolated part or function of a glass process, or to assess numerical treatments. However, many problems require the mutual interactions of several parts or processes to be considered simultaneously. A good example is a glass melting furnace, in which there exist several flow regimes, multimode heat transfer, physical and chemical reactions, and other related phenomena.

Modeling a glass melting tank provides a means to estimate the effects of many things contemplated by a glass maker. Simulations made with a properly constructed model can, for instance, assist in prescribing or changing the profiles of combustion burners, E-boost power zones, or bubbler flow rates. Changes in pull rate, insulation thickness or type, added wind cooling to outside walls, and surface treatments to alter emissivity of crown materials are just a few other examples of what can be considered with a furnace model.

The effects of various changes can be measured in different ways, too. The overall rate of energy consumption is often a key performance index (KPI). Other KPIs relate to the glass quality. For example, the distribution of residence times for material passing through the melting furnace is important to its operators because, with the shortest times, the material is least likely to have been fully conditioned and, thus, is most likely to have some sort of imperfection such as seeds or cords (Chapter 1.2). Other effects of interest include the maximum temperatures of various refractories, the shear stresses and other

Figure 5 Sketch of a glass melting furnace for the production of reinforcement fiber glass.



conditions contributing to wear, the position of the batch line, and the strength of the backflow of glass against the batch layer.

4.2.2 Interacting Zones

Within a complete furnace model (Figure 5), the common zones included are the glass melt, a batch cover and a foam layer both floating on the top surface of the glass, the hot combustion zone above the glass/batch/foam surface, and the wall zones enclosing the glass and combustion zones. Most of these zones are coupled to each other through exchange of mass, momentum, and energy. The governing equations, boundary conditions, and sources applied to each zone depend on the physical phenomena which occur within each of them, as well as the manner in which they are coupled to the others.

Glass flow in the melter is laminar so that Eqs. (1) and (5–7) apply. To account for the exponential dependence of viscosity upon temperature in a manner, the empirical Fulcher law is often used,

$$\mu = 10^{F_1 + \frac{F_2}{(T + F_3)}}, \quad (15)$$

where F_1 , F_2 , and F_3 depend on the specific glass composition (Chapter 4.1).

Glass flow is forced to a certain extent by the introduction and melting of batch as well as by draining through the throat of the furnace. However, additional forces significantly affect flow patterns. Density changes caused by temperature variations give rise to buoyancy forces, which significantly affect flow patterns in the glass melt. These are accounted for through a body force, which is the last term on the right side of each momentum Eqs. (5)–(7). It is convenient and typical for one of the coordinate directions (e.g. the z -direction) to be aligned with the direction of gravity (or at least opposite to it), so that the body force in its respective momentum equation is represented as

$$B_i = \rho(T)g_i, \quad (16)$$

where $\rho(T)$ is the local density evaluated at the local temperature and g_i represents gravitational acceleration in coordinate direction i (e.g. $g_z = -9.806 \text{ m/s}^2$).

Although the glass is heated from above, which usually results in a stable, vertical temperature gradient, freshly melted material from the batch blanket is relatively cool and dense so that it provides a significant driving force for recirculation in the melt. These buoyancy-driven recirculation velocities can be an order of magnitude larger than those resulting from the forward flow of glass associated with the melter pull. Furthermore, lateral temperature gradients along sidewalls and electrodes provide additional density variations that alter the flow structure. Accounting for flow-inducing density variations thus is essential in the glass melt.

Bubblers also induce significant recirculation of glass caused by forced convection. Buoyancy forces acting on the bubbles cause them to rise, and in doing so, they drag glass upward along with them (Chapter 1.3). With sufficient multiphase modeling techniques, it is possible to track explicitly the flow of both glass and bubbles, but one commonly treats the effects of the glass bubbles more abstractly by applying a momentum source to the appropriate component of the momentum equation in the columnar region associated with each bubbler. That is, the source term will be augmented by a calculated force per unit volume based upon either Stokes' law or a modified version of it [14].

Another means of affecting glass flow is with mechanical stirrers. These can be accounted for in several ways including appropriately scaled volumetric-source terms or through basic boundary conditions where the motion of a wetted wall is prescribed.

Other walls, such as the sidewalls, floor, and electrode surfaces, are simply treated as nonslip boundaries where the fluid velocity is zero. Along the top surface, the glass interacts with the batch, foam and possibly the

combustion fumes. Because of extreme density differences, the influences of foam and combustion fumes on the glass velocities are often assumed to be negligible. The interface between the batch and glass, however, represents a greater challenge, because the momentum exchange between these two zones is not considered negligible, and the interface itself can be difficult to define precisely. Moreover, the batch–glass interface is where freshly melted glass enters the glass domain from the batch layer. Commercial codes treat this interface in different ways. Because it is beyond our scope to cover the details, we will just note that this topic is an area of needed, ongoing development.

Equation (8) governs some of the energy transport in the glass and is the basis for which temperature distributions are determined. Sometimes an enthalpy formulation is used in place of Eq. (8) to couple intrinsically the batch and glass zones with a single equation governing energy transport, in which case temperatures are determined from enthalpy through an appropriate thermodynamic equation of state. Energy is also transported into and through the glass by electrical dissipation and thermal radiation. Joule dissipation is determined from the solution of equation (F) in Table 2. The rate of conversion of electrical energy to thermal energy is represented by the following:

$$E_J''' = \nabla E \cdot \vec{J} = k_e \nabla E^2, \quad (17)$$

where ∇E is the gradient in electric potential, $\vec{J}$ is the current flux density, and k_e is the temperature-dependent electrical conductivity of glass. The Joule dissipation calculated in this way is included in the source term, S_T , in the energy Eq. (8).

Thermal radiation is usually accounted for with the aforementioned Rosseland approximation. But a more detailed accounting of thermal radiation transport is possible with methods such as discrete ordinates, which can, for example, be used to resolve spectral characteristics. Other means are available [3].

The combustion zone above the glass is modeled with the same basic governing equations for momentum and energy conservation, but their application is different for a variety of reasons. Furthermore, transport equations for individual species and thermodynamic state relationships must be applied to account for the reaction of fuel and oxidizer and the creation of products of combustion.

Since the combustion zone is turbulent, all diffusion coefficients are replaced with effective values that account for diffusive-like transport. Hence, it is common to include the k and ϵ equations (D and E in Table 2), from which μ_t is determined. Another difference involves radiation for which the assumption of optically thick media required by the Rosseland approximation is not valid.

Use of discrete ordinates in combustion zones is common. The absorption coefficients required of the DOM depend on species concentrations, especially CO_2 and H_2O , which must be determined from a combustion model that accounts for chemical reactions (i.e. the creation and destruction of molecular species) and the transport of the related species.

Through radiative and convective transport, the combustion gases heat virtually all surfaces, including the walls of the superstructure, the top of the batch layer, the foam, and the glass. Furthermore, these surfaces exchange heat through radiation, which is intrinsically included with a discrete ordinates model. Owing to nonlinearities and to the strong coupling between the various zones and between the various transport equations within a zone, a robust, iterative solver is required to converge on a solution. Typically, iterations are performed until conservation laws are satisfied to within 0.1%, whereas adjustments to URCs are sometimes required to improve convergence.

A model of a glass melting furnace must account for transport not only in the glass and combustion zones, but also within the batch, foam, and walls. Whereas all of these zones must obey the same basic laws of physics, their dissimilar material characteristics require different mathematical treatments. Perhaps the easiest to consider are the walls and other solid objects. The energy Eq. (C) (in Table 2) is applied without the advection term since velocities in the walls are zero. Equation (F) is in addition applied to account for electrical current and Joule heating with the assumption that the electric potential is uniform within an electrode, since its electrical conductivity is orders of magnitude larger than that of any other material.

The batch and foam require additional considerations. Considering first the foam, there are many questions to ask. Where does it exist? How thick is it? Does it absorb radiation from the combustion zone and crown, or does it transmit such radiation? What is the gaseous species within the liquid glass membrane? How large are the foam cells? All of these and other factors will affect transport so that choosing a modeling method presents a significant challenge.

One way to deal with foam is to invoke several simplifying assumptions allowing adjustments based on foam conditions, without requiring detailed information regarding its phenomenological behavior. For example, foam can be treated as a layer of material that acts to impede heat transfer between combustion and glass zones, but ignores advection transport within it. A relatively small number of parameters can be used to characterize the thermal behavior of the foam, which can be adjusted, within reason, to render a well-tuned model.

A similar set of questions arises when considering the batch. Whereas the foam is a two-phase mixture of liquid membranes enclosing gas cells, the batch is a multiphase mixture of solid particles, with interstitial gas and liquid, whose proportions depend on temperature. Unlike in the foam, advective energy transport within the batch zone cannot be ignored without large compromises such that, therefore, the velocity field within the batch layer must be computed. A common way to accomplish it is to treat the batch as a pseudo-fluid with a characteristic viscosity that depends on temperature. The batch is assumed to float on top of the glass and to provide an inflow of melt whenever the temperature at its interface with the glass achieves or exceeds a specified temperature where melting occurs. In this way, the batch zone is treated as another fluid zone governed by equations similar to those of the glass. In addition to providing an inlet flow of melt to the glass zone, the batch zone also produces a small amount of gases into the combustion zone because of the chemical reactions that occur upon melting.

The model described in the preceding paragraphs is an example of a powerful tool constructed from well-defined assumptions and mathematical abstractions. It is summarized in Table 3, which indicates for each zone of the furnace the governing equations and interactions with other zones. The required boundary conditions and other physical parameters needed to specify the operating conditions are summarized in Table 4 where a “coupled” condition indicates an internal boundary condition between two zones where the field variable and associated flux are forced to be the same. In addition, many numerical parameters must be specified in such a way as to bring about a converged solution that satisfies the various conservation principles. Modeling procedures and material properties for glass are discussed in greater detail elsewhere [15].

4.2.3 Post-processing Assessments

One gains additional insights by displaying the computed field variables in a graphical form. A common illustration is a temperature-contour plot, sometimes with flow streaks superimposed. A 3-D rendering of a glass melting furnace (Figure 6.), for instance, clearly shows the batch layer that melts at the glass surface and the flame developing from the rear wall, the extent of these zones being important operational characteristics. An alternative to horizontal flames is presented in Figure 7, where the pair of flames from oxy-fuel burners yield the temperature contours and flow streaks shown for a cross-section of the combustion zone. The fuel and oxidizer react as they flow downward from their nozzles mounted in the furnace crown, and the resulting flame directly impinges on the batch and promotes improved melting efficiency. Similar plots can be drawn on different sections or in different orientations within combustion or glass zones. Furthermore, contour plots of electric potential, Joule dissipation, oxygen concentration, or other field variables can be made directly from the computed solution to provide important insights, especially when comparisons are made between plots drawn for differing possible operating conditions.

Other important information can be gleaned from a converged simulation. For example, quantified values of the energy transfers between the zones illustrated in Figure 5 can be extracted from the simulation results. Examining and comparing these values is very insightful, as it can draw the attention to various things such as how the batch is melted and the sources of inefficiency.

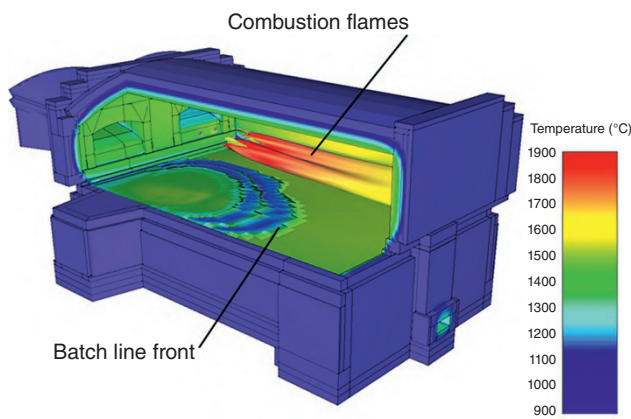
Other quantifiable data that can be directly extracted from a model solution include operating currents and potentials of electrodes, average glass temperature, total volume of batch layer, and temperatures at prescribed

Table 3 Interacting zones of a complete glass melting-furnace model.

Zone	Equations (Table 2)	Radiation treatment	Zone couplings				
			Glass	Batch	Foam	Walls	Combustion
Glass	A,B,C,F	Rosseland					
Batch	A,B,C,F	Surface emissivity	Mass, momentum, energy, electric current				
Foam	C	Surface emissivity and transparency	Energy	Energy			
Walls	C,F	Surface emissivity	Energy, electric current	Energy, electric current	Energy		
Combustion	A,B,C,D,E,G	DOM	Energy	Mass, energy	Energy	Energy	
			Glass	Batch	Foam	Walls	Combustion

Table 4 Required boundary conditions for a complete glass melting-furnace model.

Governing equation	Zone				
	Glass	Batch	Foam	Walls	Combustion
Continuity (A)	Pull rate (out) Coupled (from Batch)	Pull rate (in) Coupled (to Glass)	(no flow)	(no flow)	Fuel flow rates Oxidizer flow rates Outlet flow rate
Momentum (B)	No slip @ Walls velocity @ Batch Interface no shear @ Surface/Foam bubbler flows	Free surface @ Top no shear @ Glass interface	(no flow)	(no flow)	Inlet velocities No slip on walls, Turbulence wall functions
Energy (C)	Coupled	Batch inlet temperature Coupled	Coupled	Coupled convection and radiation on outside walls	Inlet temperatures Coupled turbulence wall functions
TKE(D)	(laminar)	(laminar)	(no flow)	(no flow)	Inlet conditions Turbulence wall functions
Turb. diss. (E)	(laminar)	(laminar)	(no flow)	(no flow)	Inlet conditions Turbulence wall functions
Electric (F)	Coupled	Coupled	(none)	Electrode voltages and phases	(none)
Species (G)	(none)	Coupled discharge to combustion zone	(none)	(none)	Mole/mass fractions of fuel and oxidizer species zero flux at walls coupled to batch discharge


Figure 6 3-D rendering of temperature contours within a glass furnace heated with two gas burners as calculated by a fully coupled simulation model. *Source:* Courtesy of Glass Service, Inc.

locations (e.g. where control or monitoring thermocouples are installed in the actual furnace). These data are essential for validating a model.

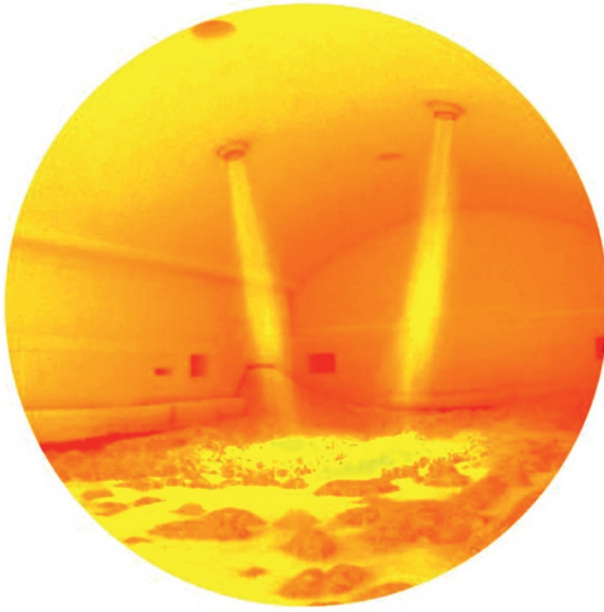
4.2.4 Particle Tracking

Additional information is provided by particle tracking and associated analysis as applied to either combustion

or glass (including batch) zones. To track the pathway, inert particles would take if they were introduced into the glass involves additional computation in a Lagrangian framework. Massless particles are commonly used as a kind of virtual flow visualization because the assumption is made that they do not affect the flow of glass. Depending only on glass velocities, their pathways can then be computed from converged solutions of glass flows. To simulate real phenomena, however, particles of specified density and size or gas bubbles can also be tracked, in which cases the velocity of each particle may differ locally from that of the glass because of the effects of gravity.

When massless particles are introduced into a melting tank through a random selection of a large number of starting locations on the batch inlets, their pathways over time can be tracked from the computed field of velocity vectors. When each particle passes through a target plane at the furnace exit, its residence time in the melter can also be recorded. A representative histogram of such times is shown in Figure 8a. The shortest are of primary interest since they are associated with portions of the glass that receive the least amount of thermal conditioning. A more detailed picture can thus be drawn from comparisons made between the pathways of particles with the shortest 0.1% and average residence times (Figure 8b–c), where the so-called short-circuit pathways of the former

(a)



(b)

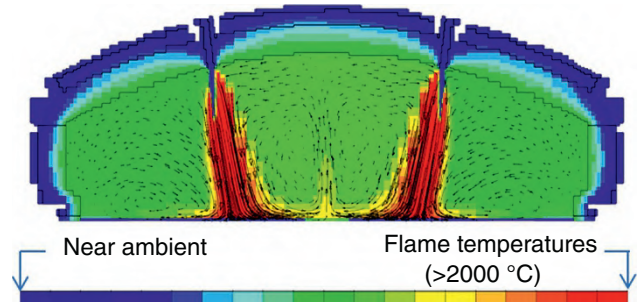


Figure 7 Combustion zone of a fiber glass melting furnace. (a) Photo of oxy-fuel flames; (b) temperature contours calculated by a simulation model.

contrast with the large recirculation loops followed several times by the latter.

Other mathematical integrations are often performed along particle paths. One example is the dimensionless mixing index, which can be interpreted as the number of times a spherical cord of glass of specified initial diameter d_{ci} would dissolve as it travels along the path of the particle, from beginning to end. This index is defined as

$$I_{mix} = \int_0^{\text{end}} \frac{4 \|\nabla \vec{V}\|^{2/3} \mathcal{D}}{3d_{ci}^{2/3}} d\tau, \quad (18)$$

where $\mathcal{D}$ is the species diffusion coefficient in glass. In a manner similar to that of residence times, a distribution of mixing indices can thus be determined from the massless particle traces, and other similar indices also be computed.

Another analysis involves tracking and particles to account for the dissolution of each particle along its pathway as shown in Figure 9 for particles emanating from the batch layer and disappearing in the glass. The top and side views shown in Figure 9 are of the same melting tank illustrated in Figure 8. A distribution of survival times, average temperatures, and final temperatures can be assembled and compared with distributions gathered from other simulations representing different conditions. Such comparisons can be useful in assessing the likelihood of introducing unmelted batch stones into the

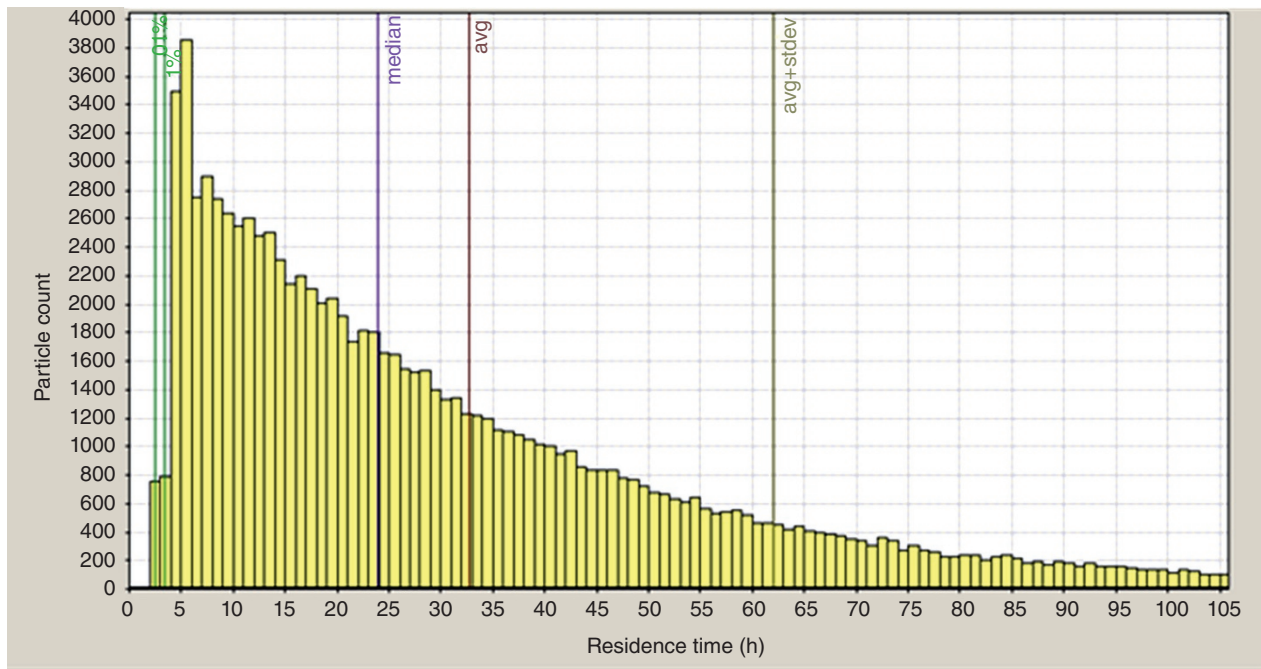
front-end. Similar tracking techniques can of course be applied to gas bubbles.

5 Simulation Data Management

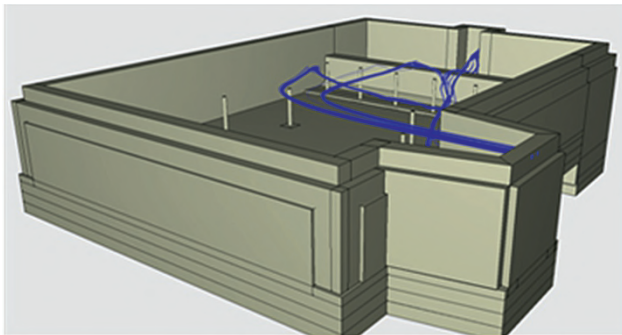
Since modeling has gained wider acceptance and is increasingly relied upon to support important decisions, capturing and cataloging simulation models, the data used for their input, and the calculated results are very important. Managing simulation data has become a challenge for many organizations engaged in process modeling. A good simulation data management (SDM) system allows models to be “recycled” and used again for a different set of operating conditions, and allows different users to access archived models and their data. Furthermore, a good system has cataloging and search features that allow users in need of modeling data to access it quickly, even if they are not familiar with the previous modeling study. That is, not only should a SDM system assist individual analysts to organize their results, but it should serve a larger enterprise, with many people in different and changing roles.

The interactions and associated transfer of information of different organizations within a glass processing enterprise are sketched in Figure 10. Whether simulations are performed to assist a technical-support team or a technology-development effort in R&D, the ultimate

(a)



(b)



(c)

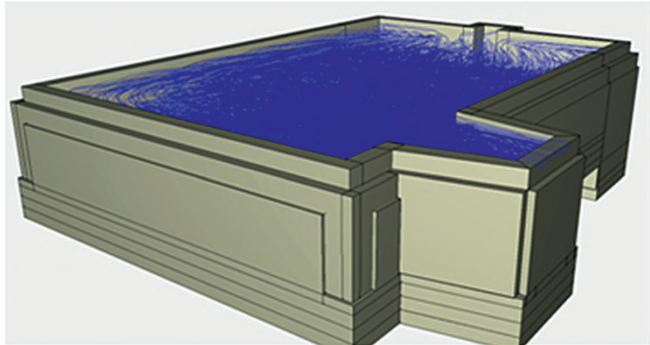


Figure 8 Results of particle tracking post-processing: (a) calculated distribution of particle residence times, (b) paths taken by fastest 0.1% particles, and (c) typical paths taken for median residence time. Same number of particles tracked in both cases. *Source:* Courtesy of Glass Service, Inc.

benefactor is the manufacturing operation. Although there are direct interactions between any two of these subgroups, an SDM system can be used to manage data collected and generated by the modeling and simulation activities.

An SDM system improves productivity by keeping data well organized and accessible to authorized individuals at various locations, who may be interested in a summary of results, build a new model based on a previous model, or mine data in search of correlations between certain operating conditions. By keeping official records, the SDM reduces problems of duplicated files or duplicated names of slightly different files. It also contributes to security by controlling access, minimizing the chance of

inadvertently deleting files, and centralizing the backup of these data.

There are numerous ways to implement some kind of SDM system, ranging from a highly structured and well-organized network-attached storage system to highly sophisticated commercial offerings that either resemble product lifecycle management (PLM) systems or are even integrated into a PLM. In addition to administering simulation data, many of these systems also can be used to manage the simulation process, where workflow is defined within collaborative groups, computational resources are shared, and sequential, parametric simulations (e.g. a design optimization exploration) can be conducted with improved effectiveness. These SDM

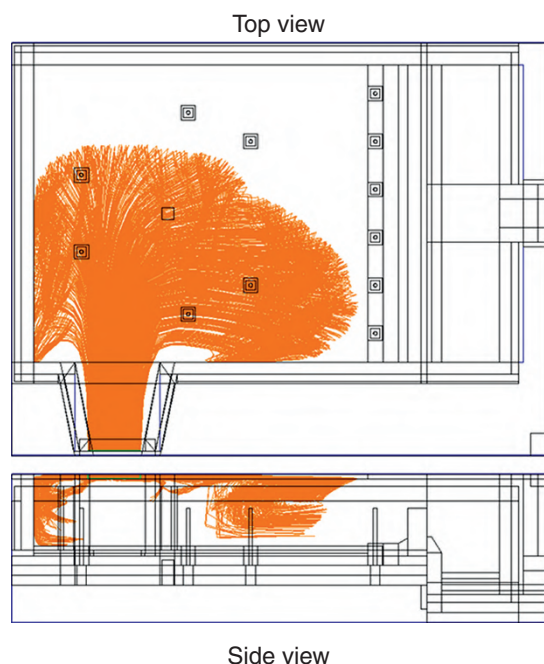


Figure 9 Pathways of sand particles dissolving in glass. *Source:* courtesy of Glass Service, Inc.

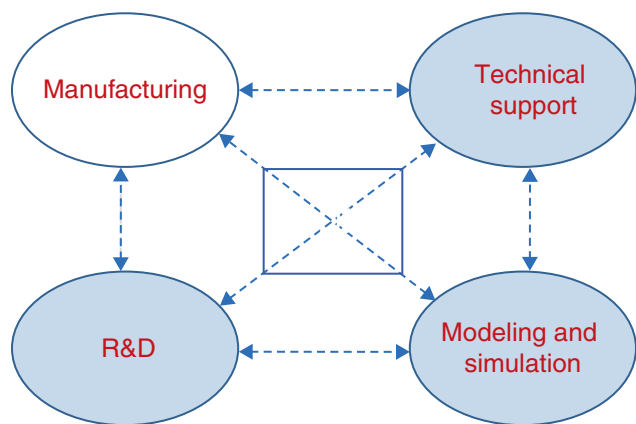


Figure 10 Central role of simulation data management in sharing of information.

systems are designed to extract metadata from model files. Examples of commonly extracted metadata are methods to characterize viscous effects (i.e. laminar, turbulent $k-\epsilon$, turbulent RSM, etc.), mesh size, mesh type (i.e. hexahedra, tetrahedral, etc.), software version, etc. For glass processing, it is possible and recommended to provide a way to extract metadata associated with the glass process; examples of these include furnace footprint size, pull rate, glass type, batch characteristics, etc. Any organization which has collaborative efforts involved with modeling and simulation should thus implement some kind of data management system.

6 Perspectives

The use of mathematical modeling in other glass industry segments has also increased over the years. Examples of such work can be found in the container, specialty, and float-glass industry for simulations of processes such as refining, homogenizing, tempering, shaping, gas generation [4, 16–18]. Striking results have, for instance, been obtained for containers for which simulations allow the shape and fabrication process to be optimized many times more rapidly (and less expensively) than in the traditional way. Not surprisingly, constructing a model to simulate a glass melting furnace is a larger, more time-consuming task. Obtaining a converged solution while considering the uncertainties associated with material properties is also challenging. Small changes to a validated model can be applied, however, and new simulation results can be computed quickly.

The amount of information that can be extracted from simulation results is appreciated for its value in assessing conditions not possible without computational modeling. Sometimes, a particular post-processing analysis is not desired until well after a simulation has been completed (i.e. weeks, months, or years later), but as long as the simulation data has been preserved, the analysis can be completed quickly.

Although advanced, modeling and simulation of glass processes can be improved. Some of the improvements are related to numerical implementation, but it is often the case that required transport properties cannot be measured without inordinate expense. Some improvements are related to achieving more accurate solutions, whereas other are related to improve post-processing. For example, improved knowledge of heat transfer in a foam could significantly reduce the time required to tune and validate a simulation model (i.e. improved accuracy and efficiency), whereas more information about refractory dissolution or wear could improve post-processing assessments of furnace life.

The batch layer represents an important area whose physics needs to be better understood. The effects of batch constituents (as well as the size and shape of individual particles), the manner in which the batch moves, transmits energy, reacts, and melts into glass need to be understood in a way that can be implemented in a numerical simulation. A similar comment can be made for foam. Despite these shortcomings, simulation results are very useful when applied and interpreted properly. When significant uncertainties exist or if validation fails to reconcile all metrics satisfactorily, then comparisons between simulations cases can be made in a semiquantitative manner, where the simulation results reveal general trends (e.g. increased recirculation, or lowering of exhaust gas temperatures). Results such as these provide guidance that would otherwise be unavailable.

Acknowledgements

The authors thank Glass Service Inc. for sharing nonproprietary model data from which some of the examples presented were taken. Also, they are grateful to their employer, Owens Corning, for supporting their effort to contribute to this volume.

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Section II. Structure

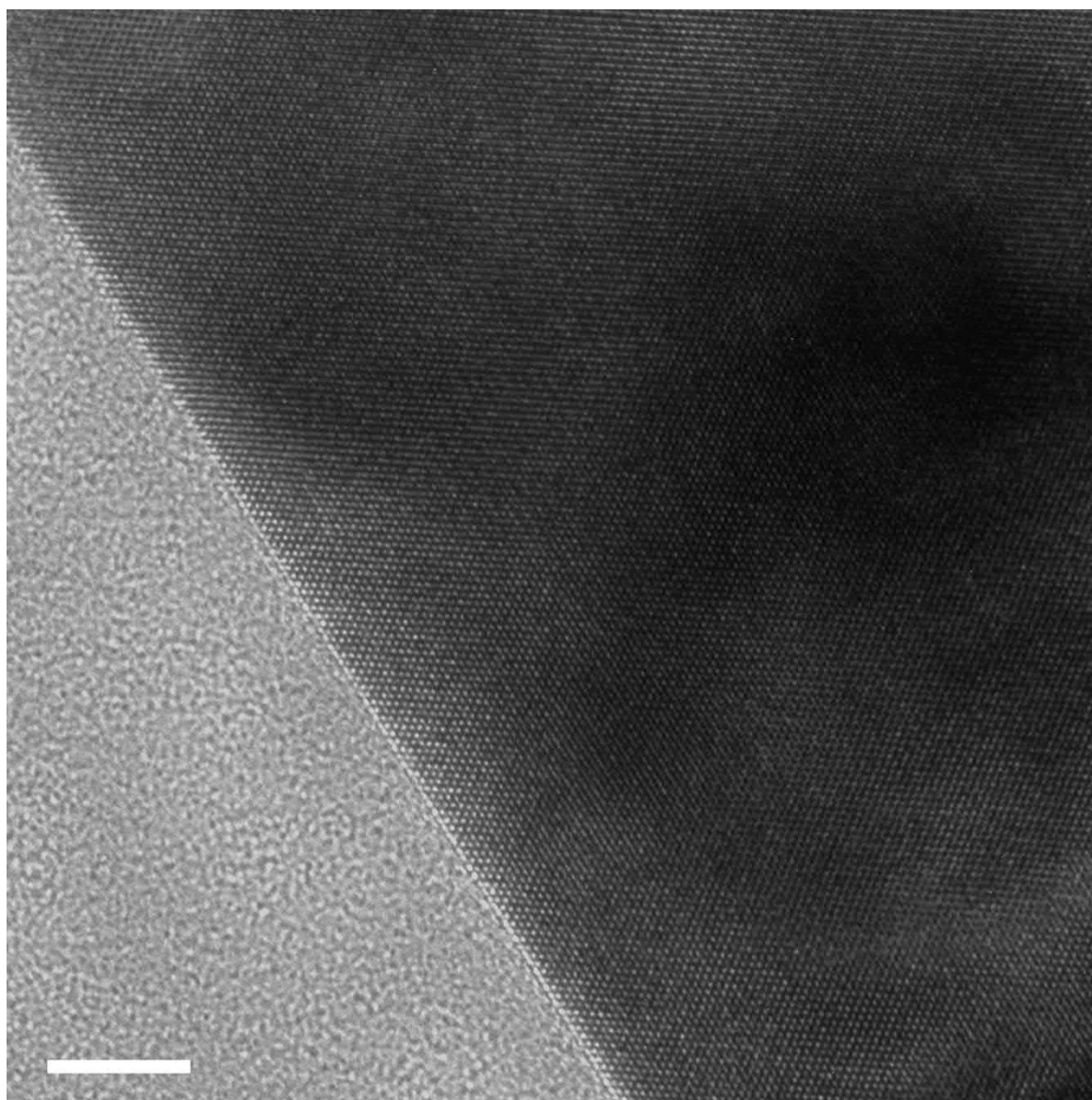


Figure 1 The atomic disorder of the glass structure (left) giving way to crystalline order (right): the boundary between a Zr-bearing magnesium aluminosilicate glass and a ZrO₂ crystal that precipitated in it. Bar scale: 5 nm. Abberation-corrected, high-resolution transmission-electron micrograph courtesy Christian Patzig and Thomas Höche.

It is usually stated that the various properties of glasses and melts are determined by the structures of these phases. This statement is thermodynamically incorrect: a melt has a structure that is fixed instead by the minimum of its Gibbs free energy and, thus, by the temperature-dependent balance between enthalpy and entropy factors that are themselves determined by the existing atomic interactions. This is the manner in which the structures of *melts* predicted in theoretical calculations are assumed to be those of *glasses* quenched from some pressure and high temperature.

Structural studies are nonetheless useful either at a small scale, for example, to figure out how the local environment of an ion determines its optical properties (Section VI), or at a larger scale to gain insights on property–composition relationships when the specific influence of chemical entities on the properties of interest can be evaluated in terms of well-defined structural elements such as rings or coordination polyhedra. The method was pioneered in Antiquity by Plato (–428–347): to each of the four elements then acknowledged, he assigned geometrical shapes accounting for their properties, namely the tetrahedron for fire, octahedron for air, icosahedron for water, and cube for earth. Of course, such assignments are no longer purely intellectual constructs; they have an experimental basis. Interestingly, however, one should realize that the first atomic models of glass were devised shortly before any experimental tool was available to determine their structural components (Chapter 10.11). In other words, glass structure represents a good example of a situation where theory not only preceded experiments but also defined their paradigmatic framework.

To set the frame of this second section of the Encyclopedia, a broad overview of the structure of amorphous materials and of associated theoretical models at different length scales is first given by A.C. Hannon for network oxide and chalcogenide glasses, with particular emphasis on the random-network model (Chapter 2.1). Recently, progress in the analytical techniques used in structural studies has been enhanced by the availability of intense sources of electromagnetic radiation, namely lasers and synchrotron facilities. From X-ray diffraction and absorption to vibrational and Mössbauer spectroscopies, these various methods and the information they yield are reviewed by G. Henderson (Chapter 2.2). Whether purposely produced in glass ceramics or formed spontaneously in industrial or natural processes, inhomogeneous glasses are also given increased attention (Figure 1). To determine their microstructure and analyze their constituents at a scale down to the nm range, C. Patzig and T. Höche then present scanning and transmission electron microscopy, analytical tools, and the relevant analytical tools and other ancillary techniques available (Chapter 2.3).

From the results obtained with these methods, the next three chapters focus on the glass structure. Short-range order is dealt with by J.F. Stebbins in a chapter where he defines such concepts as network formers and modifiers, bridging and nonbridging oxygens and their tetrahedral distribution around the network-forming cations they coordinate, and he also discusses how they change with temperature and composition (Chapter 2.4). From the scale of atoms to that of macroscopic bodies, the increasing complexity found at longer distances is then examined by G.N. Greaves who also points out the basic differences found between oxide and metallic systems (Chapter 2.5). Because glasses have generally complex chemical compositions in both industrial and geological contexts, the relationships between the structures of simple and multicomponent systems are finally described by B.O. Mysen in a perspective aimed at understanding composition–property relationships (Chapter 2.6).

Returning to more theoretical aspects, the next chapter by P.K. Gupta stresses with the *constraint theory* the importance of simple topological considerations and of temperature-dependent bond strengths to understand the glass structure and composition–property relationships. To conclude this section, two chapters review the rapid advances made in the growing field of atomistic simulations in two complementary ways. In the Monte-Carlo and molecular-dynamics simulations presented by A. Takada (Chapter 2.8), the interatomic potentials used to simulate the structure and properties of glass-forming systems are determined a priori, with the advantage that up to a few thousand particles can be considered with current computing power. As reviewed by W. Kob and S. Ispas, atomic interactions are determined instead from first principles in the more fundamental and precise *ab initio* approaches, such as density functional theory; the price is that only relatively small systems can be currently investigated (Chapter 2.9). Ascertaining the energetics of a glass-forming melt is fraught with considerable difficulties, however, because phase transformations, in which one is interested, are driven by small differences of typically a few kJ between the very large numbers yielded with significant uncertainties by *ab initio* methods.

Throughout this section the emphasis is generally put on oxide glasses. Metallic glasses are specifically dealt with in Chapter 7.10 and organic polymers in three other contributions (Chapters 8.8–8.10).

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2.1

Basic Concepts of Network Glass Structure

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1 Introduction

What is a *glass* from a structural standpoint? There are different answers dependent upon whether the emphasis is on structure, preparation methods, or thermodynamic properties. However, a simple structural definition is adopted here, according to which a material must be solid and have a noncrystalline structure to be called a glass.

Put simply, the description of a crystal involves a unit cell, containing a particular arrangement of atoms, which is then replicated periodically in three dimensions to build up the structure as illustrated by the 2-D (two dimensional) representation of Figure 1. Crystal structures have translational symmetry because, if crystallite boundaries are neglected, the environment of a particular atom is the same as that of all equivalent atoms in all unit cells. Contrastingly, a glass lacks translational symmetry and a detailed understanding of its structure requires as much experimental information as possible. In addition to X-ray (XRD) and neutron (ND) diffraction, inelastic neutron scattering and various other spectroscopies (X-ray absorption, infrared, Brillouin, Mössbauer, and X-ray photoelectron spectroscopies) may be used (Chapter 2.1), along with electron microscopy, physical property data (especially density), and theoretical modeling.

As is clear to any reader of this *Encyclopedia*, many types of materials can vitrify if they are solidified rapidly enough to avoid crystallization. Leaving aside metallic glasses (Chapter 7.10) or organic polymers (Chapters 8.7 and 8.8), however, the majority of useful glassy materials are formed by oxides or chalcogenides. This is the reason why this chapter is restricted to these materials and to the elementary concepts that are used to describe their structure.

These structures can be understood well in terms of the continuous random network (CRN) model, first propounded by Zachariasen [1], because the atomic bonds have some covalent (directional) character. The basic features of this model will thus be reviewed and related to fundamental structural information gathered for silica glass, the archetypal glass former, and the “mother” of all amorphous silicates. Because microcrystalline descriptions of glass structures in fact preceded Zachariasen’s model, their basic limitations will also be summarized. The structural changes induced by the addition of so-called network modifiers in oxide glasses will then be discussed at short- and medium-length scales, along with the intermediate character of some oxides that may act as glass formers only when combined with some modifiers. Finally, the manner in which network glasses can depart from Zachariasen’s model will be illustrated with chalcogenides.

List of Acronyms

2-D	two dimensional
BO	bridging oxygen
CRN	continuous random network
FSDP	first sharp diffraction peak
IRO	intermediate-range order
LRO	long-range order
MD	molecular dynamics
MRN	modified random network
MRO	medium-range order
NBO	non-bridging oxygen
ND	neutron diffraction
NMR	nuclear magnetic resonance
RMC	reverse Monte Carlo
SRO	short-range order
v-SiO ₂	vitreous SiO ₂
XRD	X-ray diffraction

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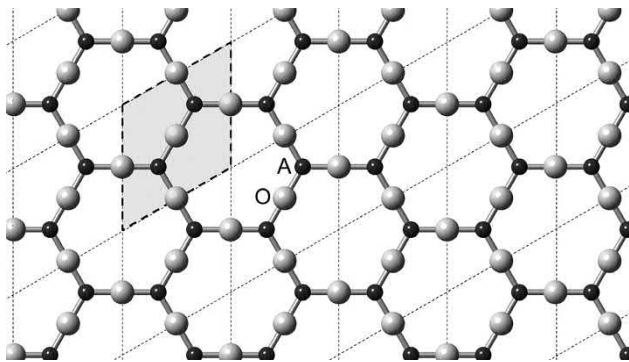


Figure 1 Two-dimensional representation of a crystal structure for a composition A_2O_3 . Small dark spheres: A atoms; large light spheres: oxygens. Unit cell delineated by thick, dashed lines.

2 The Zachariasen–Warren Random Network Model

The structure of oxide and chalcogenide glasses is usually described by the Zachariasen–Warren random network model, thus termed because it was proposed by Zachariasen [1] in 1932 and subsequently supported by early XRD studies of glass structure made by Warren and coworkers (Chapter 10.11, [2]).

This model is easily understood with reference to the structure of a 2-D A_2O_3 oxide glass (Figure 2), where the local structure is very well defined in terms of rigid triangular AO_3 units within which there is almost no variation in the bond lengths and angles. The way in which the units connect together to form a noncrystalline structure is described by a set of rules for glass formation, postulated by Zachariasen:

- 1) An oxygen atom (O) is not linked to more than two network-forming cations (A).
- 2) The coordination number, n_{AO} , of oxygen around the network-forming cations must be small, i.e. 3 or 4 (where the coordination number of an atom simply means the number of other atoms that are within a certain distance from it).
- 3) The oxygen polyhedra should share corners with each other, not edges or faces.
- 4) For a three-dimensional network, at least three corners of each polyhedron must be shared.

For the 2-D illustration of Figure 2, the coordination number for the triangular AO_3 units is three, thus satisfying the second rule. Two AO_3 units are connected to each other by the sharing of a common oxygen atom, so that the first rule is satisfied. The third rule is also satisfied, since each pair of connected units shares only one common oxygen, not two (edge-sharing), or three (face-sharing). Even though this example is a 2-D structure, it

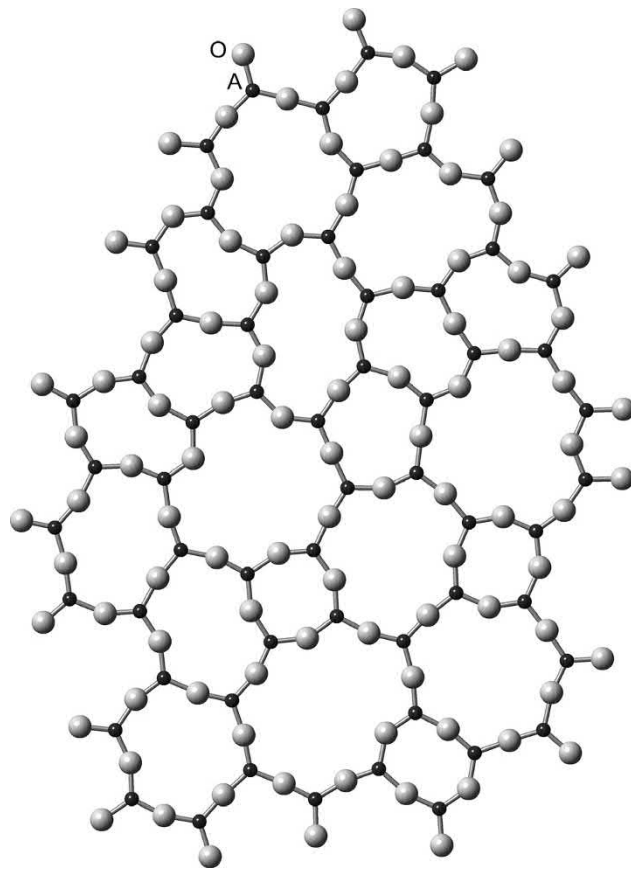


Figure 2 Two-dimensional representation of a random network for a composition A_2O_3 [1]. Small dark spheres: A atoms; large light spheres: oxygens.

also satisfies the fourth rule, since the AO_3 units are three-connected. In fact, it is well established that real glasses such as B_2O_3 [3] and As_2O_3 [4] can form three-dimensional structures based on three-connected structural units.

It should be emphasized that the random nature of the structure does not arise from disorder within the basic structural units because the distributions of bond lengths and bond angles within them can be very narrow, as in a crystal structure. Instead, there is a wide distribution of bond angles (e.g. $A-\hat{O}-A$ in Figure 2) leading to a distribution in sizes and shapes of the rings formed by the connections between the AO_3 units. The noncrystalline nature of the structure arises from this wide distribution of bond angles.

As will become clear later, not all real network glasses obey all of Zachariasen's rules. Nevertheless, these rules provide a basic philosophical framework and a valuable starting point from which the structure of real glasses can be described.

A comparison of the crystalline structure of Figure 1 with the random network of Figure 2 shows the similarity

and difference between the two. Both types of structure have *short-range* order (SRO) when distances similar to the bond lengths are considered. In fact, SRO arises naturally from the finite sizes of atoms and their mutual bonding so that it exists in all condensed phases, be they liquid, glassy, or crystalline. The fundamental difference is that only crystals exhibit *long-range* order (LRO), extending over distances that are large compared to interatomic spacings (Figure 1), whereas glasses (Figure 2) and liquids are by definition isotropic because their structure is on average the same in any direction.

3 Silica – The Archetypal Glass

Vitreous silica, $v\text{-SiO}_2$, is the archetypal example of an oxide glass. Its basic structural unit is a highly regular tetrahedron, with a silicon atom at the center and an oxygen atom at each of the four vertices, which is denoted as $\text{SiO}_{4/2}$ because each oxygen is bonded to two different silicons. The Si–O bonds are all very close in length to 1.608 Å [5], and the O–Si–O bond angles are all very close to the ideal tetrahedral value of 109.47° . Because $\text{SiO}_{4/2}$ tetrahedra are connected together by the sharing of a bridging oxygen (BO) atom (Figure 3), the Si–O–Si bridge is characterized by three angles: the Si–O–Si bond angle, θ , and the two torsion (dihedral) angles, δ_1 and δ_2 . There is a broad distribution of bond angles (centered at $\sim 144^\circ$), but little or no preference for any particular value of the torsion angle. Hence, the tetrahedra connect together to form a network that is both *continuous* (i.e. it can fill all of three-dimensional space without a break in the continuity of the network) and *random* (i.e. it is

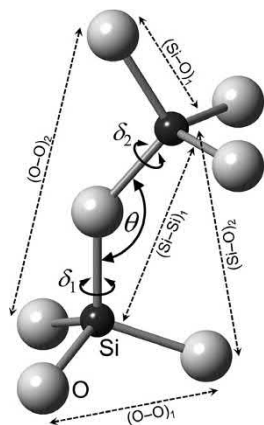


Figure 3 Connection of two corner-sharing $\text{SiO}_{4/2}$ tetrahedra by a bridging oxygen, defining the Si–O–Si bond angle, θ , at the bridging oxygen, and the torsion (or dihedral) angles for the two tetrahedra, δ_1 and δ_2 . Small dark spheres: silicons; large light spheres: oxygens. Shortest interatomic distances indicated by dashed arrows.

not periodically repeating and, thus, not crystalline). This is why a structure of this type is often called a CRN.

Initially, it was not clearly established whether a CRN constructed in this way could indeed fill three-dimensional space without the development of strains or the eventual breaking of bonds. An important step thus occurred in the 1960s when the construction of large ball-and-stick models showed that it is indeed possible to build a large tetrahedral network that is both continuous and random. The most influential was constructed by Bell and Dean [6] for silica with a total of 614 atoms (Figure 4), which appeared to form a three-dimensional CRN structure through the sharing of oxygen bridges between $\text{SiO}_{4/2}$ tetrahedra (Figure 4, inset). Ball-and-stick methods of modeling the atomic structure of glasses are rarely used nowadays, and computer-based methods are extensively used, for example, Monte Carlo, molecular dynamics (MD), or reverse Monte Carlo (RMC) simulations (Chapter 2.8, [7]).

Experimentally, evidence for a random SiO_2 network is provided by the diffraction patterns measured by both XRD [2, 8] and ND [5, 9], which has some advantages over XRD for the study of disordered materials (Chapter 2.2). Whereas the peaks observed in the diffraction patterns of

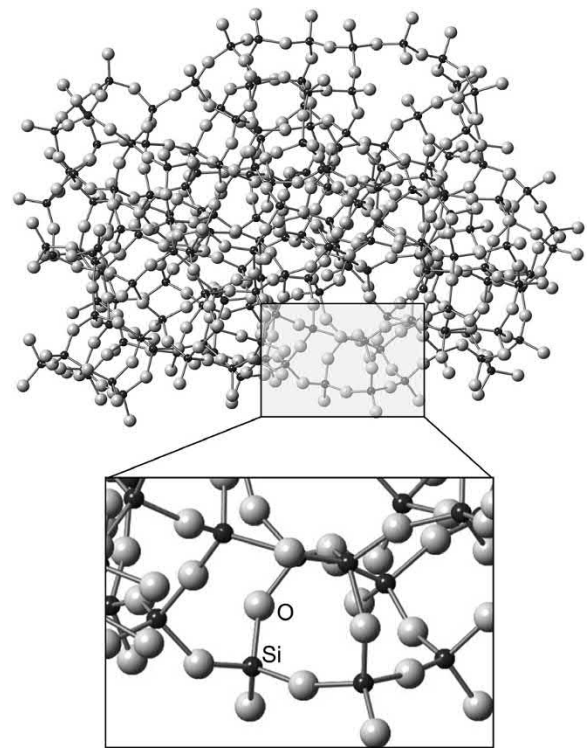


Figure 4 Ball-and-stick model constructed by Bell and Dean for SiO_2 glass [6]. Upper part: complete 614-atom model; lower part: small portion with higher magnification. Small dark spheres: silicons; large light spheres: oxygens.

crystals are sharp, those for glasses are broad (Figure 5a). These patterns are conventionally displayed as a function of momentum transfer, Q , otherwise known as the magnitude of the scattering vector. A standard analysis [10] is to obtain a correlation function from a suitable Fourier sine transform of the experimental data from reciprocal to real space (Figure 5b). The result essentially shows the distribution of interatomic distances in the measured sample, each of its peaks corresponding to a commonly occurring interatomic distance. For $v\text{-SiO}_2$, the first two peaks in the correlation function arise from the Si—O bond length and the O—O distance within $\text{SiO}_{4/2}$ tetrahedra, respectively. Since these peaks are as sharp

as for α -quartz, both distances are as well defined in the glass as in the crystal. Within the limits of what is achievable experimentally, the Si—O and O—O coordination numbers determined from the areas of these peaks are essentially four and six, as expected for a fully connected CRN of $\text{SiO}_{4/2}$ tetrahedra (Figure 3).

Because of LRO, there are further sharp peaks at longer distances in the correlation function of a crystal (Figure 5b). In contrast, these features rapidly become less well defined for a glass so that it becomes harder to determine structural information involving longer correlation lengths. For instance, the third peak in the function of $v\text{-SiO}_2$ arises from the two silicon atoms in a

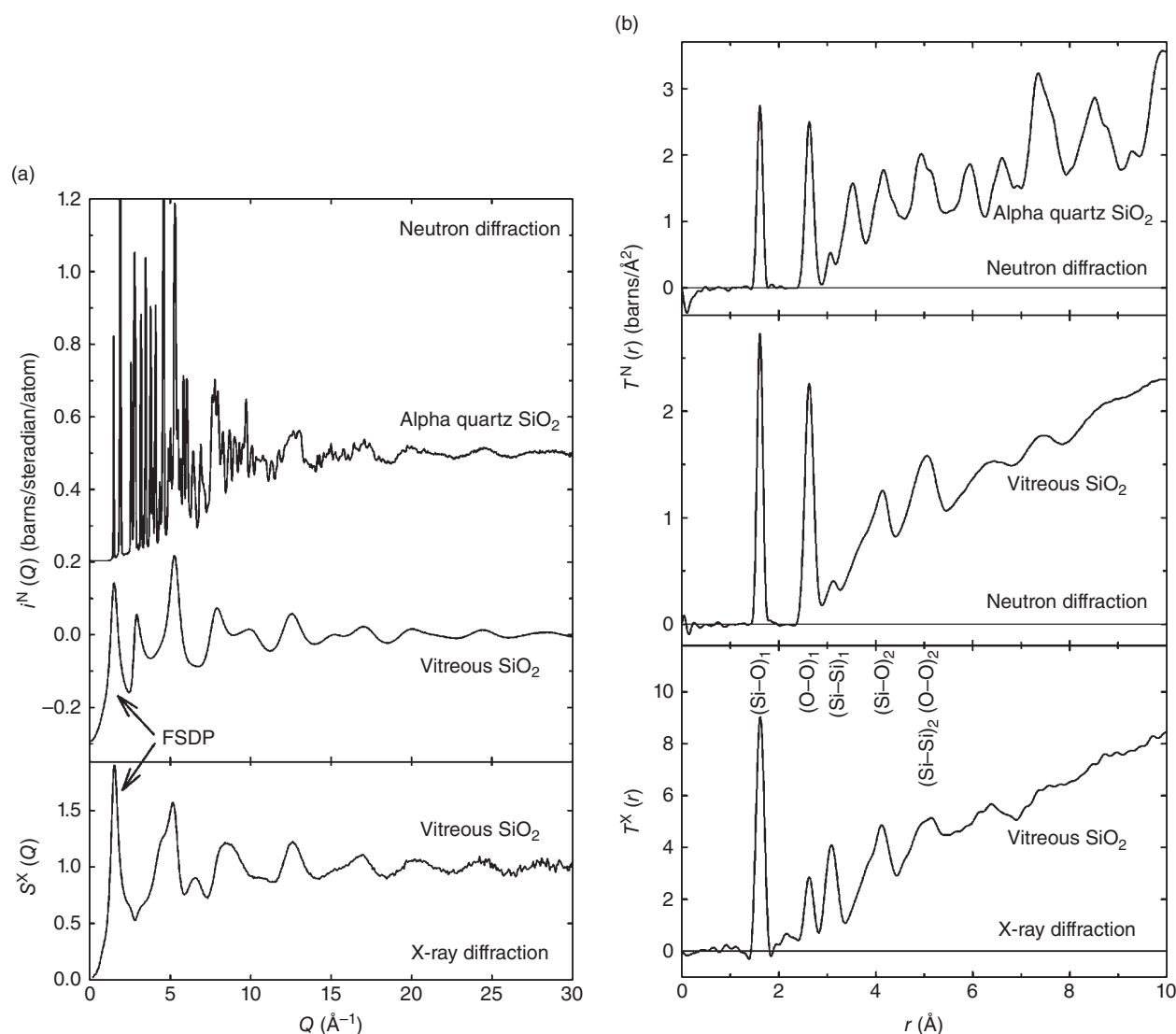


Figure 5 Diffraction results for α -quartz and $v\text{-SiO}_2$. (a) Neutron diffraction measurements of their distinct scattering [9] compared with the X-ray diffraction data for $v\text{-SiO}_2$ [8]. Position of the first sharp diffraction peak indicated at $Q_1 \approx 1.52 \text{ \AA}^{-1}$. (b) Neutron correlation function for α -quartz and $v\text{-SiO}_2$, and X-ray correlation function for $v\text{-SiO}_2$. Approximate positions of the short distances for a pair of connected tetrahedra indicated as $(\text{Si-O})_1$, and so on (same notation as in Figure 3).

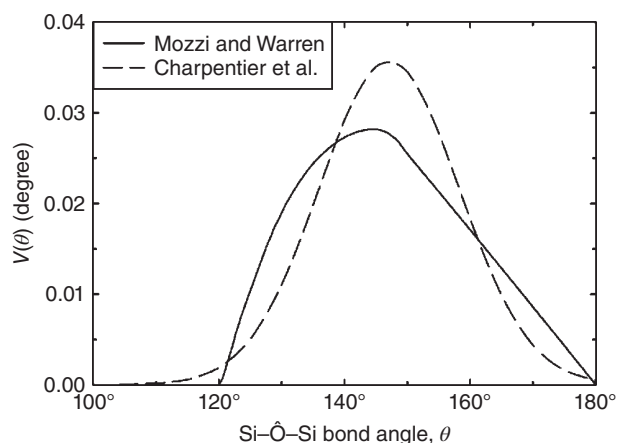


Figure 6 Comparison between the Si—O—Si bond angle distributions, $V(\theta)$, in SiO_2 glass, obtained from an analysis of the X-ray correlation function [11] (continuous line) and in a recent NMR study [12] (dashed line).

connected pair of $\text{SiO}_{4/2}$ tetrahedra. This peak is broadened due to variations in the angle θ (Figure 3), which lead to the random nature of the structure. The distribution of Si—O—Si bond angles, θ , has been extensively investigated. From fits made to their X-ray correlation function, Mozzi and Warren [11], for instance, found a most probable bond angle of 144° with an average value of 147.9° and a standard deviation of 12.7° (Figure 6). In a recent nuclear magnetic resonance (NMR) study, a narrower distribution was deduced with values of 147.1 and 11.2° , respectively [12].

A nice example of the structural information that can now be drawn from advanced forms of microscopy is provided by v- SiO_2 . For example, the amorphous region of a 2-D layer of SiO_2 on a graphene support has recently been imaged at the atomic scale (Figure 5b in Chapter 2.5). A bi-tetrahedral layer is visible in the image where the nodes are the locations of Si atoms. Hence, the view is that of a layer of faces of tetrahedra whose similarity with the 2-D representation of a random network shown in Figure 2 is striking.

4 Microcrystalline Models

Early in its study, the structure of silica glass was described in terms of the so-called microcrystalline model [13], and hence it is useful to mention it briefly here. Its starting point is that, although crystals have diffraction peaks that are much narrower than for glasses (Figure 5a), significant broadening is observed if crystallites are very small, in accordance with the Scherrer equation, $\Delta Q = 2\pi K/L$, which relates the width of a Bragg peak

ΔQ to the crystallite dimension L and to a shape factor K (~ 1).

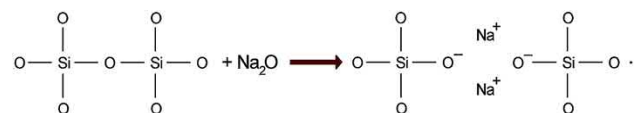
To account for its broad diffraction peaks, one might thus describe a glass in terms of very small crystallites. However, a problem with the model is that to explain the large widths of the observed glass diffraction peaks, the crystallite size should typically be on order of $5 \text{ \AA}$, a value similar to unit-cell dimensions. Philosophically, it makes no sense to consider crystallites as ordered entities if they contain only one unit cell, since there would be no translational symmetry. Furthermore, with such small crystallites, a crystalline powder would be composed almost entirely of grain boundary material, which by definition differs structurally from the bulk. Hence, microcrystalline models cannot provide a description of the structure of most of the material in the glass. For these two reasons, they need not be considered further.

5 Modifiers and Non-Bridging Oxygens

5.1 The Role of Network Modifiers

The only oxides that can readily form glasses on their own are SiO_2 , GeO_2 , B_2O_3 , P_2O_5 , and As_2O_3 . They are known as glass or network *formers*. Their structures are well described as random networks (Figures 2 and 4), involving well-defined oxygen coordination polyhedra, namely $\text{SiO}_{4/2}$ tetrahedra (Figure 7c), $\text{GeO}_{4/2}$ tetrahedra (Figure 7c), $\text{O}=\text{PO}_{3/2}$ tetrahedra (Figure 7d), $\text{BO}_{3/2}$ triangles (Figure 7a), and $\text{AsO}_{3/2}$ trigonal pyramids (Figure 7b). The ability to vitrify readily arises as a consequence of the network structure.

If a second oxide with weaker, ionic bonding is added, then it can lead to some depolymerization of the network, as shown schematically for Na_2O by the following reaction.



The additional oxygen introduced as Na_2O is accommodated in the network by the breaking of bridges; a single BO, bonded to two silicon atoms, is replaced by two non-bridging oxygens (NBOs), each bonded to one silicon atom. In this depolymerization reaction, the NBOs are shown with a negative charge, balancing the positive charges on the Na^+ cations. As sketched in a 2-D representation (Figure 4 of Chapter 2.4), such second oxides modify the network structure of the glass former, but do not become part of the network itself, hence their name of *modifiers*. Alkali and alkaline earth oxides are the most

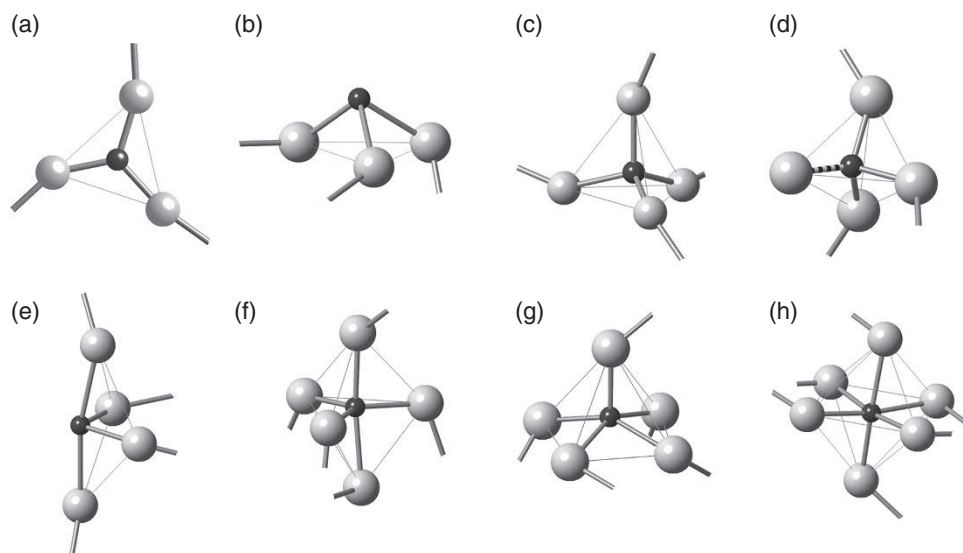


Figure 7 Structural units in network glasses: (a) $\text{AO}_{3/2}$ triangle; (b) $\text{AO}_{3/2}$ trigonal pyramid; (c) $\text{AO}_{4/2}$ tetrahedron; (d) $\text{O}=\text{PO}_{3/2}$ tetrahedron (double bond $\text{P}=\text{O}$ shown dashed); (e) $\text{AO}_{4/2}$ pseudo-trigonal bipyramid (disphenoid); (f) $\text{AO}_{5/2}$ trigonal bipyramid; (g) $\text{AO}_{5/2}$ square pyramid-based unit; (h) $\text{AO}_{6/2}$ octahedron.

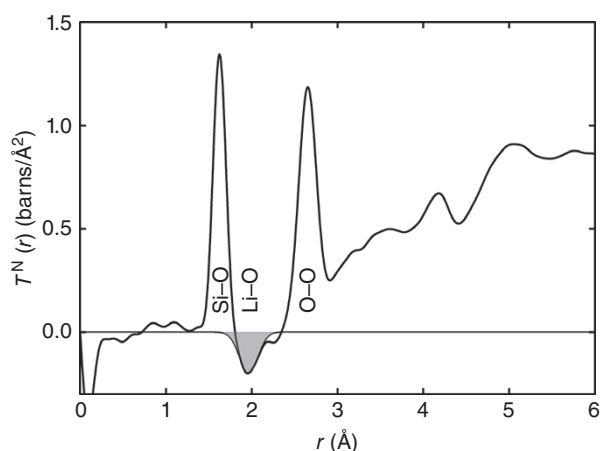


Figure 8 Neutron correlation function for lithium disilicate glass [14]. The $\text{Li}-\text{O}$ shaded peak is negative, making it readily identifiable in comparison with the positive $\text{Si}-\text{O}$ and $\text{O}-\text{O}$ peaks (Figure 5b).

common examples. They cannot form a glass by themselves, but only in combination with a glass former.

This structural view emerged from early XRD studies where the modifier cations M were regarded as being stuffed into available holes in the network. However, subsequent studies have shown that modifiers actually have a well-defined coordination shell with a fairly narrow distribution of $M-\text{O}$ bond lengths, as exemplified in Figure 8 by the neutron correlation function for lithium disilicate glass where the $\text{Li}-\text{O}$ bond peak is clearly apparent [14]. In contrast, however, there is little

evidence that the oxygen coordination polyhedra of modifier cations generally have a well-defined geometry, which would involve a narrow distribution of $\text{O}-\hat{M}-\text{O}$ bond angles.

Glass formers have strong bonds and a low coordination number, the tetrahedral value of four being the most common, whereas modifiers have weak bonds and coordination numbers typically greater than four. These high values, combined with a lower cation charge, mean that $M-\text{O}$ bonds are much weaker and, hence, that all glass properties are profoundly altered by the introduction of modifiers. For example, the addition of Na_2O generally reduces viscosity, glass transition temperatures, and melting conditions.

There are other oxides known as *conditional* glass formers, because their structural role is intermediate between those of formers and modifiers. They do not readily form a glass on their own, but can readily do so in combination with a modifier as, for example, has been known for over a century for Al_2O_3 in $\text{CaO}-\text{Al}_2\text{O}_3$ melts. In addition to Al_2O_3 , other notable conditional glass formers are Ga_2O_3 , Sb_2O_3 , TiO_2 , TeO_2 , V_2O_5 , Nb_2O_5 , and Bi_2O_3 . Because they have a geometrically well-defined coordination shell, conditional glass formers give rise to structures that are well described as random networks. For instance, the networks formed by binary aluminate and gallate glasses are based on $\text{AlO}_{4/2}$ and $\text{GaO}_{4/2}$ tetrahedra (Figure 7c), respectively. On the other hand, in more complex systems involving a glass former, aluminum can occur with mixed four-, five-, and six-coordination as clearly revealed by ^{27}Al NMR spectra,

which are very sensitive to Al speciation. Antimonite glasses form a network based on $\text{SbO}_{3/2}$ trigonal pyramids (Figure 7b). Contrastingly, tellurite glasses form a network based on two different units, $\text{TeO}_{4/2}$ pseudo-trigonal bipyramids (or disphenoids, Figure 7e) and $\text{TeO}_{3/2}$ trigonal pyramids (Figure 7b). Similarly, vanadate glasses involve a mixture of VO_4 and VO_5 units (Figure 7f and g). Also, binary niobate glasses seem to be dominated by five-coordinated NbO_5 units. In alkali titanate glasses, the network is formed from $\text{TiO}_{4/2}$ tetrahedra, although five-coordinated $\text{O}=\text{TiO}_{4/2}$ units (cf. Figure 7g, but with a terminal apical oxygen) and octahedral TiO_6 units (Figure 7h) can be found in more complex glasses.

As listed in Table 1, the most commonly studied oxides can thus be classified structurally according to their role in the formation of glass networks [15]. This classification is not exact, but nonetheless represents a useful guide; for example, TeO_2 and Sb_2O_3 have been classified as conditional glass formers, but actually both vitrify if quenched rapidly enough. Besides, some oxides with a lone-pair cation, such as PbO , are listed as both a modifier and a conditional glass former. Depending on whether or not the lone-pair of electrons is stereochemically active, the oxide acts as a network former (with a low coordination number) or as a modifier (with a high coordination number).

5.2 The Modified Random Network Model

In the aforementioned depolymerization reaction, an NBO is conventionally depicted with a negative charge to balance the positive charge on the Na^+ modifier cation, shown to indicate ionic bonding between the anions and cations. Although this reaction only shows two NBOs adjacent to the Na^+ , the coordination numbers of modifier cations are actually larger, typically greater than four.

Table 1 Structural classification of commonly studied oxides in glasses. Frequently found M—O coordination numbers (where M indicates the cation) are given in brackets.

Glass formers (network formers)	Intermediates/Conditional glass formers	Network modifiers
B_2O_3 (3,4)	Al_2O_3 (4,5,6)	Li_2O (4,5)
SiO_2 (4)	Ga_2O_3 (4,5,6)	Na_2O (4–7)
GeO_2 (4,5,6)	Sb_2O_3 (3,4)	K_2O (5–9)
P_2O_5 (4)	TiO_2 (4,5,6)	Cs_2O (6–12)
As_2O_3 (3)	TeO_2 (3,4)	MgO (4,5)
	V_2O_5 (4,5)	CaO (~6)
	Nb_2O_5 (5)	SrO (4–7)
	Bi_2O_3 (4–6?)	ZrO_2 (~6)
	ZnO (4)	MnO (4–6)
	PbO (3,4,5)	PbO (6–12)
	SnO (3,4,5)	SnO (6–12)
	Ti_2O (~3)	Ti_2O (6–12)

It is thus inevitable that the modifier cations are clustered in some way. According to Greaves' modified random network (MRN) model (Chapter 2.5), the modifiers coalesce into channels if their content exceeds a percolation limit. There are thus two interlacing sublattices: the network regions constructed from network formers and the inter-network regions made up of modifiers (see Figure 8a in Chapter 2.5). Such a microstructure has important consequences for the physical and transport properties (e.g. ionic conductivity).

5.3 Network Connectivity and Q-species

In pure SiO_2 glass, all silicon atoms are bonded to four BOs. However, as a modifier is added, the average number of BOs bonded to a silicon decreases, and there is a corresponding increase in the number of NBOs bonded to a silicon. Experimental evidence indicates very strongly that all of the silicon atoms remain tetrahedrally coordinated in almost all silicate glass systems. Thus, when a modifier is added, there is a mixture of Q^n tetrahedra, where n and $4 - n$ are the numbers of BOs and NBOs bonded to the silicon, respectively (cf. Chapter 2.4). Hence, Q^4 represents a silicon atom bonded to four BOs (as in pure SiO_2 glass), Q^3 a silicon atom bonded to three BOs and one NBO, and so on. The abundances of these species can be quantitatively determined by ^{29}Si NMR measurements as illustrated in Figure 9 for lithium silicate glasses [16]. The distribution of Si sites between the different Q^n -species is not statistically random, but, to first approximation, follows instead a binary rule: the addition of small amounts of modifier to the glass leads to the conversion of Q^4 to only Q^3 until composition $J = \text{Li}_2\text{O}/\text{SiO}_2 = 0.5$, equivalent to 33.3 mol % Li_2O , is reached, at which all silicons are on Q^3 sites; then follows a region of composition $0.5 < J < 1.0$, where the addition of more modifier leads to the conversion of Q^3 sites to only Q^2 , and so on. This evolution has important consequences for the connectivity of the silicate network. For example, a glass with a majority of Q^2 sites is dominated by chains (or isolated rings) of silicon tetrahedra. When $J > 1.0$ (i.e. for less than 50 mol % SiO_2), the 3-D connectivity of the structure breaks down. These materials are known as *invert* glasses since their structure is dominated by the bonds to the modifier cations, thus inverting the roles of these cations.

5.4 Change of Coordination Number

A detailed discussion of bonding and the manner in which it determines atomic coordination numbers and polyhedra is beyond the scope of this chapter. Although of very limited practical use, the 8- N rule provides a very simple illustration of an approach to bonding. It states

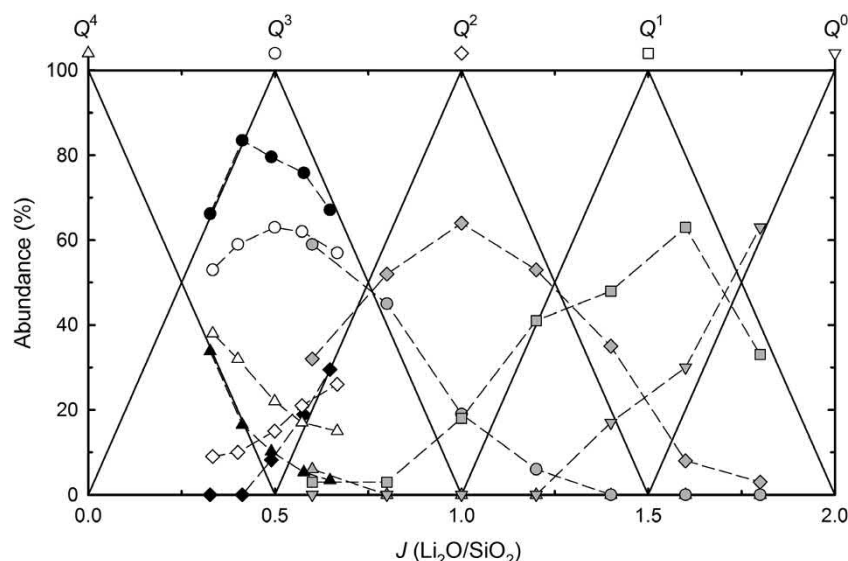


Figure 9 Deviations of the relative abundance of Q^n -species in lithium silicate glasses (points) from an idealized binary distribution (continuous lines) as a function of the $\text{Li}_2\text{O}/\text{SiO}_2$ ratio, J [16]. Shading of the points indicating the original ^{29}Si NMR experimental data (see key on the figure):

$\triangle$ - Q^4 , $\circ$ - Q^3 , $\diamond$ - Q^2 , $\square$ - Q^1 , ∇ - Q^0 .

that the coordination number of a covalently bonded atom with N valence electrons is $8-N$. Now, the electronic configurations of silicon and oxygen are $[\text{Ne}] 3s^2 3p^2$ and $[\text{He}] 2s^2 2p^4$, respectively, so that with 4 and 6 valence electrons these elements should have coordination numbers of 4 and 2, respectively, as actually observed in $\nu\text{-SiO}_2$ and in silicate glasses at zero pressure. Silicon atoms with a higher coordination number do occur, but usually under high pressure, the only known exception being alkali phosphosilicate glasses (e.g. $\text{Na}_2\text{O-P}_2\text{O}_5\text{-SiO}_2$), in which the presence of some six-coordinated silicon has been established [17].

For other glass formers, a higher cation coordination can in contrast occur with ease. For example, in pure B_2O_3 glass, all boron atoms are three-coordinated, as depicted for a fragment of the network in Figure 10a. However, there are two alternative ways in which a modifier such as M_2O may be accommodated in a borate network. The additional oxygen from a M_2O unit can be incorporated into the network either by conversion of one BO to two NBOs (Figure 10b), as occurs in silicates, or by conversion of two borons from three- to four-coordination (Figure 10c). Because ^{11}B NMR is sensitive to the presence of four-coordinated boron, the average coordination number, n_{BO} , can be measured over very wide composition ranges. For $x\text{Li}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ glasses (Figure 11), n_{BO} increases with x , from 3 for B_2O_3 itself, to a maximum value of 3.44 ± 0.01 at 35–38 mol % Li_2O , and then falls for further increases in the Li_2O content [18].

This variation can be reasonably accounted for by a simple charge-avoidance model [19], in which additional oxygen is incorporated into the borate network by the conversion of BO_3 units to BO_4 provided that centers of negative charge are not directly connected. These

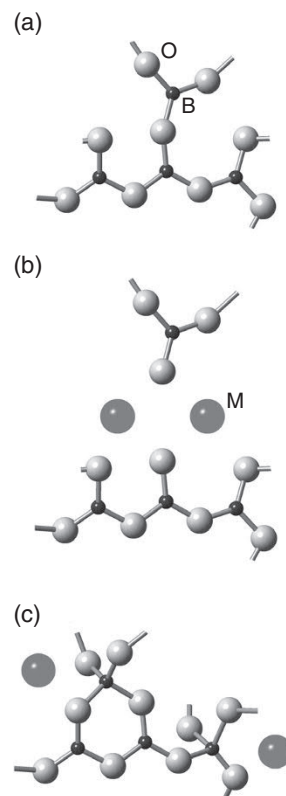


Figure 10 The two differing effects of the addition of a network modifier cation M^+ on the borate network. (a) Fragment of the network of pure B_2O_3 glass (small spheres are B atoms, and large spheres are O atoms). (b) Formation of non-bridging oxygens. (c) Formation of four-coordinated boron atoms.

centers are not only NBOs but also BO_4 units since these have a net negative charge. For small amounts of modifier, the formation of BO_4 units causes n_{BO} to be equal

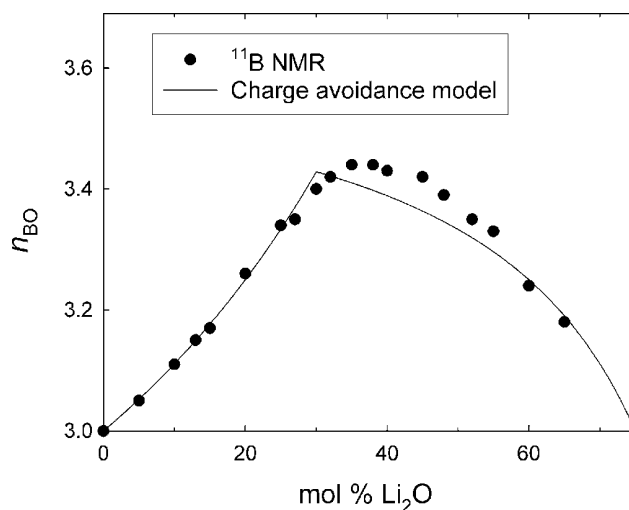


Figure 11 Boron-oxygen coordination number, n_{BO} , for lithium borate glasses, $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, as determined by ^{11}B NMR (points) [18], compared with the prediction from a charge-avoidance model [19].

to $3 + x/(1 - x)$. At larger contents, however, NBOs form instead so that n_{BO} falls back toward a value of three. Similarly, the thermophysical properties of borate glasses show a maximum (or minimum) as modifier is added to the glass known as the *borate anomaly*.

Pure germania glass, GeO_2 , forms a tetrahedral network, similar to that of silica, but with a smaller average $\text{Ge}-\text{O}-\text{Ge}$ bond angle. As for borates, however, the addition of a modifier is accompanied by a growth and then a decline in the value of the average coordination number, n_{GeO} , and the thermophysical properties also show a maximum (or minimum). Originally, this *germanate anomaly* was ascribed to the formation of octahedral (i.e. six-coordinated) germanium atoms. Compared to the borate anomaly, however, evidence concerning the structural aspects of the germanate anomaly is much less plentiful because germanium nuclei are not usefully accessible to NMR. For cesium germanate glasses, ND measurements [20] show that as Cs_2O is added to GeO_2 glass, n_{GeO} increases up to a maximum value of 4.36 for 18 mol % Cs_2O , and then falls for further increases in the Cs_2O content (Figure 12). The additional oxygen from an M_2O unit can lead to a growth in n_{GeO} either by converting one GeO_4 into a GeO_6 unit, or by converting two GeO_4 units into GeO_5 units, and both mechanisms are possible in principle. However, the variation of n_{GeO} for cesium germanates is much better predicted by a charge-avoidance model if the higher germanium coordination number is five, rather than six. Nevertheless, evidence is beginning to emerge that the preferred higher Ge coordination in germanate glasses may depend on the modifier cation.

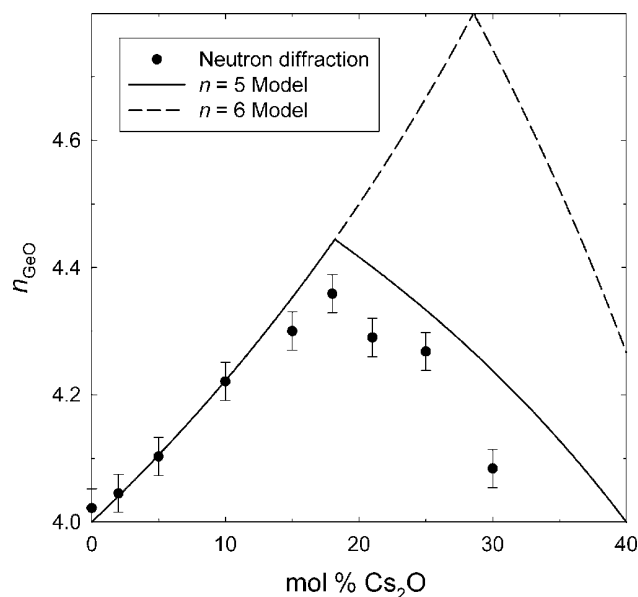


Figure 12 Germanium-oxygen coordination number, n_{GeO} , for cesium germanate glasses, $\text{Cs}_2\text{O}-\text{GeO}_2$, as determined by neutron diffraction [20], compared with the predictions of charge-avoidance models in which the higher GeO_n coordination is either 5 or 6.

6 Intermediate-Range Order

Until this point, only SRO has been discussed, along with the structural characteristics that arise directly from interatomic bonding, namely bond lengths, coordination numbers, bond angles, and coordination polyhedra. Even though LRO is by definition lacking in glasses, some ordering exists at length scales between SRO and LRO. It is known as *intermediate-* or *medium-range order* (IRO or MRO).

It must be acknowledged that IRO is much harder to probe experimentally than SRO and is, therefore, much less well known. To investigate it, structural modeling may in fact be required to complement direct experimental evidence. This order can be variously characterized in terms of clustering (e.g. Greaves' MRN, cf. Figure 8a in Chapter 2.5) or free volume, for example, but the most widespread approach is to consider the rings that are defined by connected polyhedra in the CRN. Whereas a crystal contains only very few different rings (e.g. the 2-D crystal of Figure 1 contains only six-membered rings), the rings in a CRN have a wider and more varied distribution of sizes (Figures 2 and 4).

Although this ring-size distribution in general cannot be directly addressed experimentally, there are some notable exceptions. A case in point is v-SiO_2 , whose Raman spectrum shows two sharp peaks, at 495 and 606 cm^{-1} , known as D-lines, because they were initially

assigned as defect modes. It is now clear, however, that they represent instead the breathing modes of highly regular four-membered rings and planar three-membered rings, respectively [21]. Although these modes give rise to distinctive peaks in the Raman spectrum, theoretical analysis shows that the concentrations of these highly regular rings are actually low, with fractions of oxygens in regular four-membered rings and planar three-membered rings estimated as 0.36% and 0.22%, respectively [22].

Likewise, borate networks exhibit different rings of $\text{BO}_{3/2}$ and $\text{BO}_{4/2}$ units, which have no (or very few) internal degrees of freedom, and thus have very clear signatures in vibrational spectra. The best known is the boroxol group, a highly planar ring of three $\text{BO}_{3/2}$ units, which was first detected in B_2O_3 glass (Chapter 10.11). Much experimental evidence from a number of techniques [3] shows that in B_2O_3 glass about 75% of boron atoms are in boroxol groups, while the remainder are in individual $\text{BO}_{3/2}$ triangles. The boroxol group is in fact so well defined that it can be regarded as a larger structural unit, a superstructural unit, as illustrated in a 2-D representation of the structure of B_2O_3 glass (Figure 13). As a modifier is added to B_2O_3 , boroxol groups become less abundant, but they are replaced by other types of borate superstructural units [19].

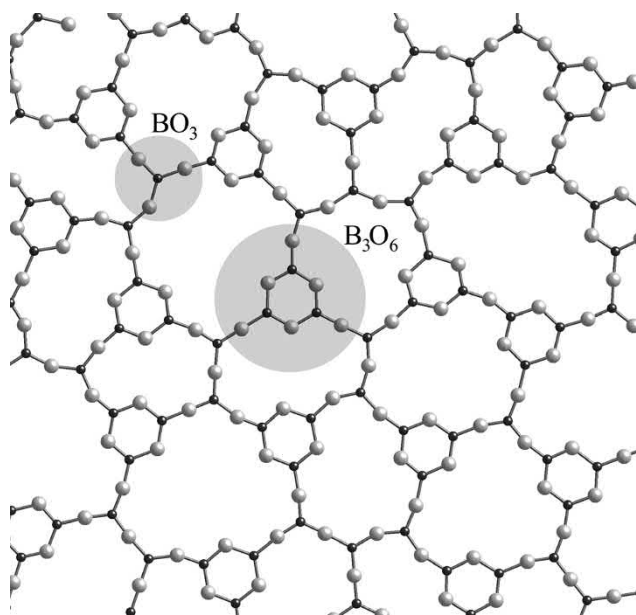


Figure 13 Two-dimensional representation of the boroxol ring model for the structure of B_2O_3 glass [3]; a randomly ordered network of boroxol groups and independent BO_3 triangles. Shaded areas indicating a typical boroxol group (B_3O_6) and independent triangle (BO_3), respectively.

Another approach to IRO is to study the first peak in the diffraction pattern, the so-called first sharp diffraction peak (FSDP), see Figure 5a. The FSDP has been treated as especially important by many workers, perhaps because it is related to the order with the longest period in real space. However, Salmon has pointed out that the longest range ordering in glasses actually gives rise to the second peak in the diffraction pattern (the so-called principal peak) [23]. In the past, it was often popular to regard the FSDP as evidence of crystal-like layers in the glass, because the peak position, Q_1 , is similar to the position of the first (00ℓ) reflection arising from layers in a closely related crystalline phase. However, it is now clear that the FSDP arises from correlated voids in the network [24]; a more easily understood view of this idea is to regard the FSDP as arising from the approximate repetition of the walls of the three-dimensional cages formed by the CRN [25].

7 Chalcogenide Glasses

Although chalcogenide glasses, i.e. glasses containing one or more chalcogenide elements, sulfur, selenium, and tellurium, but no oxygen, are dealt with in Chapter 6.5, it is useful to discuss them briefly here because their random network structures differ from those of oxides by contravening Zachariasen's rules for glass formation.

Oxide glasses are completely ordered chemically, so that bonding occurs only between unlike atoms, i.e. oxygen anions only bond to cations, and cations only bond to oxygens. This is not the case for chalcogenide glasses, in which like atoms can bond. For example, in Ge—Se glasses, homopolar Ge—Ge or Se—Se bonds coexist with heteropolar Ge—Se bonds. In contrast to the single stoichiometric SiO_2 composition of silica glass, chalcogenide glasses form over a wide compositional range, as exemplified by $\text{Ge}_x\text{Se}_{1-x}$ glasses, which form in the range $0 < x < 0.42$. Some homopolar bonds are found even at the stoichiometric composition GeSe_2 , as depicted in Figure 14 where the connectivity of a fragment of a Ge—Se network is sketched: Ge atoms are tetrahedrally bonded to four other Se or Ge atoms, whereas Se atoms are bonded to two other Ge or Se atoms. Nevertheless, there is a strong preference for chemical order so that the measured coordination numbers for the Ge—Ge and Se—Se homopolar bonds in GeSe_2 are 0.25 and 0.20, respectively [26]. In Figure 14, the number of homopolar bonds has thus been exaggerated for the purpose of illustration.

Another difference from oxide glasses is that edge-sharing may occur between the structural units. For example, in Ge—Se glasses, a significant number of $\text{GeSe}_{4/2}$ tetrahedra share an edge with another

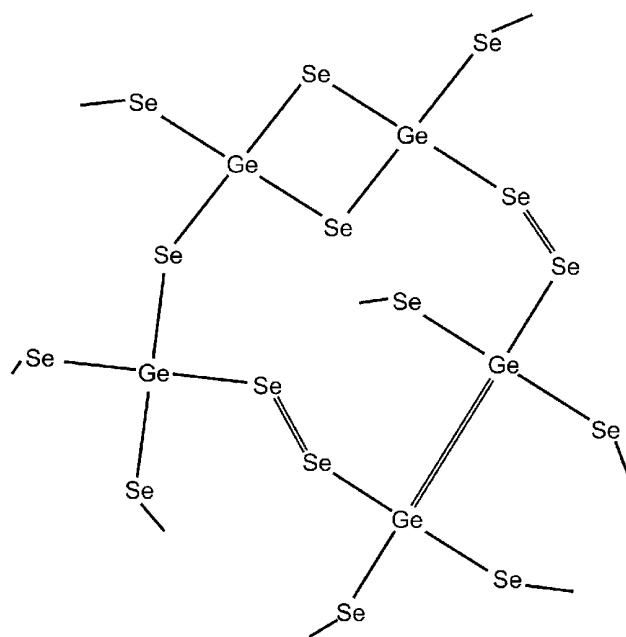


Figure 14 Network connectivity for a Ge—Se glass with a composition close to GeSe_2 . Pair of edge-sharing $\text{GeSe}_{4/2}$ tetrahedra shown at the top of the figure. Homopolar Ge—Ge and Se—Se bonds represented by a double line.

tetrahedron (see Figure 14), the proportion being 34% in GeSe_2 glass [26]. A noteworthy consequence is the existence of unusually short Ge—Ge distances, which are readily observed by diffraction and also, thanks to a specific vibrational mode, by Raman spectroscopy. Furthermore, some chalcogenide glasses contain molecular units as well as network material. For example, As—S glasses with high S content contain sulfur rings, such as S_8 , while As—S glasses with high As content (~40 at. % As) contain entities such as the As_4S_4 molecule that constitutes the mineral realgar, and others.

This variable composition of chalcogenide glasses leads to variations in the connectivity of the network, and hence in the rigidity of the network. It is predicted by constraint theory (see Chapter 2.8) that the network undergoes a transition from a floppy state to a rigid state when the average coordination number increases through a value of about 2.4 [27], with a major influence on the physical properties.

8 Perspectives

For crystalline materials, the structure is formed from exact repetitions of a huge number of identical (or almost identical) unit cells. Thus, for the most part, a structure solution simply requires the determination of the positions of the relatively very small number of atoms in

the unit cell. The methods of crystallography are immensely powerful so that diffraction methods are pre-eminent in this respect.

Contrastingly, glass is by definition noncrystalline. To determine the statistical distributions of its structural parameters, such as bond length, bond angle, ring size, and so on, structural studies have few of the advantages enjoyed by crystallographers for crystals. Because the amount of information that can be obtained from a single experiment on a glass is small, structural studies are much slower to proceed for glasses than for crystals, and researchers have to fight for each grain of information. In view of this challenge to obtain reliable information, in past decades it has been necessary for researchers to become expert in a particular experimental technique to achieve reliable progress. Nowadays, however, not only are most experimental probes of glass structure well established but their capabilities are steadily being improved as well. It is thus becoming possible to use a number of experimental methods well, so that significant progress is likely to be made by the increasing application of multi-technique methods to the same set of glass samples; for instance, a combination of ND, XRD, NMR, and Raman scattering can reveal a more complete description of the structure of a glass. With the steady improvement of experimental methods and their interpretation, and such a growing use of multiple techniques, it is likely that gradually more complex glasses will be studied with a growing resolution, and that modeling will have in parallel an increasingly significant role in improving our understanding of glass structure.

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2.2

Structural Probes of Glass

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1 Introduction

The atomic arrangements that make up the structure of a condensed phase can be probed only with particles or electromagnetic radiation that penetrate into the material and interact with its atoms in such a way that analysis of the changes they undergo yield the specific information sought after. Probably the most basic information is relative atomic positions, which can be derived from X-ray and neutron diffraction experiments because groups of atoms may act as gratings with respect to radiation whose wavelengths are in the Ångström-range of interatomic distances. Alternatively, all other structural probes rely on the exchange of electromagnetic energy in certain frequency ranges to yield information not on the bulk structure of the material, but on individual types of atoms or groups of atoms. As a first example, absorption of X-rays by electrons at eV-energies probes the effects of interatomic bonding on the electronic levels of a given atom and, thus, the environment of this atom and even its redox state. As a second example, similar information may be derived for appropriate transition metal elements with Mössbauer spectroscopy from interactions at higher energies of gamma rays with atomic nuclei. A summary of the methods presented in this chapter along these lines is given in Table 1.

Regardless of the method used, probing atomic structure is much easier for crystals than for amorphous materials. To “solve” the structure, one only requires knowledge of the unit cell as defined by the crystallographic axes (a , b , c) and angles (α , β , γ), the lattice type (P, F, I, A, B, C, H, R), the symmetry associated with both the unit cell (point group) and the lattice (space group),

and the positions of the atoms relative to the origin of the unit cell. One *does not need* to determine the position of *all the atoms* in the structure, but only the minimum number required by the point group symmetry.

Solving the structure of an amorphous material such as glass, on the other hand, currently is not possible and is unlikely in the foreseeable future because of the lack of long-distance atomic periodicity. Hence, one cannot define a unit cell, a lattice, or their associated symmetry that would enable reproduction of the positions of atoms without having to determine the explicit location of all the atoms in three-dimensional space. In essence, *glasses have an infinite unit cell* so that “solving” the structure would require knowledge of the position of every atom, an impossible task.

Nevertheless, it is possible to probe a great many structural features if one keeps in mind that the discrete values of interatomic angles and distances existing in crystals give way in glasses to continuous distributions that can be characterized by their shapes, widths, and maximum or averaged values. In addition to these parameters that characterize the bulk structure of the glass, information pertaining to specific atoms can also be gathered, such as the coordination polyhedra of the various constituents of the material.

Because the structure of a glass represents that of the solid “frozen-in” at the glass transition, it is also important to investigate the marked temperature-induced structural changes that take place in melts at higher temperatures. In this regard, two cases should be distinguished depending on the differences between the experimental timescale of the method and the rate of structural change of the melt. If the former is very short with respect to the latter, then the result will be a snapshot of a solid-like structure; if it is long, the result will represent a time-averaged structure that brings little information on the individual features that are averaged (see Section 4).

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Table 1 Summary of techniques used to determine various features of glass structure.

Technique	Energy (eV)	Frequency (Hz)	Wavelength (nm)	Process	Information obtained
X-ray diffraction	0.1–100 keV	3×10^{16} – 3×10^{19}	0.01–10 nm	Scattering/diffraction from electrons	~0–15 Å, quantitative bond lengths and angles over short- and intermediate-range length scales
Neutron diffraction	0.1–500 meV	0.04–120 THz	0.04–3 nm	Scattering/diffraction from neutrons	~0–15 Å, quantitative bond lengths and angles over short- and intermediate-range length scales, dynamics
EXAFS	0.1–100 keV	3×10^{16} – 3×10^{19}	0.01–10 nm	Atom-specific absorption of X-rays, multiple scattering	~5–6 Å, quantitative atom-specific bond lengths and coordination
XANES	0.1–100 keV	3×10^{16} – 3×10^{19}	0.01–10 nm	Atom-specific electronic transitions to unoccupied orbitals, multiple scattering	~1–3 Å, qualitative coordination, oxidation state, electronic structure
XRS	Usually <10 keV	2.4×10^{13} – 3.4×10^{17}	~1–1000 nm	Energy loss of inelastically scattered X-ray photons	<i>In-situ</i> high-pressure energy loss spectra of low z elements (equivalent to XANES), short-range structure, electronic structure
XPS	~0.1–1400 eV	2.4×10^{13} – 3.4×10^{17}	~1–3000 nm	Energy of ejected core and valence electrons	Oxygen speciation (BO, NBO, free oxygen)
EELS/ELNES	10 meV–10 keV	7.2×10^{11} – 2.9×10^{17}	~1–1000 nm	Energy loss of transmitted electrons through the sample	Same as XANES
IR	886 meV–3eV	430×10^{12} – 300×10^9	1 mm–2500 nm	Molecular vibrations	Vibrational states, quantification of CO ₂ /H ₂ O in glasses, coordination states, short- and intermediate-range structure
Raman	1.2–120 meV	3×10^{11} – 1.5×10^{14}	0.5 mm–1000 nm	Molecular vibrations, inelastic photon interactions	Vibrational states, Q species, ring statistics, short- and intermediate-range structure
Brillouin	1.2×10^{-3} – 7.4×10^{-4} eV	10^7 – 1.8×10^{11}	100–1000 nm	Inelastic photon–phonon interactions	Elastic and acoustic properties
UV/Vis	1.7–124 eV	30×10^{19} – 790×10^{12}	10–700 nm	Valence electron transitions	Oxidation and coordination states of transition metals
NMR	12.4 peV–1.24 meV	3×10^3 – 300×10^9	~1 km–1 mm	Nuclear spin interactions	Short- and intermediate-range structure, bond angles, coordination states, Q species, dynamics
Mössbauer	100 keV	$>10^{19}$	<0.1 nm	Nuclear transitions	Oxidation state and coordination of Mössbauer active nuclei: typical Fe, Sn in glasses

In order to select the most suitable technique for probing the glass of interest, one has to determine what aspect of the structure is to be probed (bulk or atom specific), and what is the length scale to be probed (short-range, intermediate-range, or extended-range)? In many instances more than one technique will need to be employed. I will briefly discuss a number of common and not so common techniques for deriving structural information on glasses. Whereas space constraints limit the detail that can be provided, I will provide a general overview of what aspect of the structure is probed and what information can be determined from each method. The reader should refer to any of a number of detailed reviews of the specific techniques currently available (e.g. [1, 2]).

Acronyms

3Q	triple quantum
AFM	atomic force microscopy
AWAXS	anomalous wide angle X-ray scattering
BE	binding energy
BO	bridging oxygen
CN	coordination number
DAXS	diffraction anomalous X-ray scattering
EELS	electron energy-loss spectroscopy
ELNES	energy loss near-edge spectroscopy
eV	electron volt
EXAFS	extended X-ray absorption fine structure
FID	free induction decay
FSDP	first sharp diffraction peak
FT-IR	Fourier transform infrared
FWHM	full width at half maximum
HRTEM	high-resolution transmission electron microscopy
IR	infrared
IRO	intermediate-range order
IS	isomer shift
IVCT	intervalence charge transfer
keV	kilo electron volt
KK	Kramers–Krönig
LO	longitudinal optic
LRO	long-range order
MAS	magic angle spinning
MD	molecular dynamics
MQ	multiple quantum
NBO	non-bridging oxygen
NMR	nuclear magnetic resonance
NRIXS	non-resonant inelastic X-ray scattering
PDF	pair distribution function
PSF	partial structure factor
QS	quadrupole splitting
RDF	radial distribution function

RF	radio frequency
RMC	reverse Monte Carlo
SRO	short-range order
TO	transverse optic
TSF	total structure factor
UV	ultra violet
Vis	visible
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRS	X-ray Raman spectroscopy

2 Diffraction (Scattering)

2.1 X-ray and Neutron

Neutron and X-ray diffraction are two of the principal techniques used to probe the bulk structure of glasses through determination of average bond lengths, coordination numbers (CN), and angles over both the short (nearest neighbors) and intermediate (next-nearest neighbors) length scales. Data analysis and interpretation are comparable for X-ray and neutron diffraction so that I will differentiate between the two methods only when needed. In passing, note that in earlier studies the interaction between the X-rays and the sample was termed scattering, and not diffraction as made now.

For X-rays, diffraction experiments are readily made but they are not well suited to discriminate between neighbor atoms in the periodic table, such as silicon and aluminum, because of the similar electronic clouds with which X-rays interact in these cases. Thanks to their lack of electrical charge, neutrons are (with neutrinos) the only particles that can penetrate a condensed phase. They do not interact with electronic clouds, but are diffracted by atomic nuclei because they are strongly sensitive to nuclear forces. If both methods are available, the choice of X-ray or neutron diffraction depends to some extent on the chemical composition of the glass. Neutrons are, for instance, better suited than X-rays for investigating light elements such as H and they have the advantage of providing better spatial resolution and allowing more detailed information to be obtained through isotope substitution methods, which rely on the fact that neutron diffraction is sensitive to the neutron content of a nuclei. Practical factors have also to be taken into account: intense sources are much more widely available for X-rays than for neutrons, whereas the required sample sizes are of the order of 1 mg and 50 g, respectively. The samples themselves may be in the form of powders, glass chips, or shaped glass chips.

The “diffraction pattern” of a glass is very different from that of a crystal (cf. [3]). A crystal will produce a series of “spots” or “reflections” on a two-dimensional diffraction image or sharp diffraction lines on a powder diffraction trace. These cannot be seen in the diffraction image of a glass. This contrast is illustrated by the area electron-diffraction images of a crystalline material ($\text{Ba}_2\text{TiGe}_2\text{O}_8$, Ge-substituted fresnoite) and of an amorphous material ($\text{Ba}_2\text{TiSi}_2\text{O}_8$, fresnoite glass) shown in Figure 1a, b. Clearly, no “reflections” are observed in the glass image. A similar contrast is seen between an X-ray powder diffraction trace

of quartz (crystalline SiO_2) and that of the glass plate on which the quartz sample was mounted (Figure 1c, d). Note the very weak intensity, lack of diffraction peaks (reflections), and low signal-to-noise ratio of the glass trace. Where there is a “diffraction peak,” it has weak intensity and is extremely broad and diffuse, which is characteristic of a material lacking periodic structure.

Each reflection in a crystal image represents coherent diffraction from a plane of atoms whose intensity depends on the nature of these atoms. The “diffraction pattern” of a homogeneous glass will exhibit no such reflections but

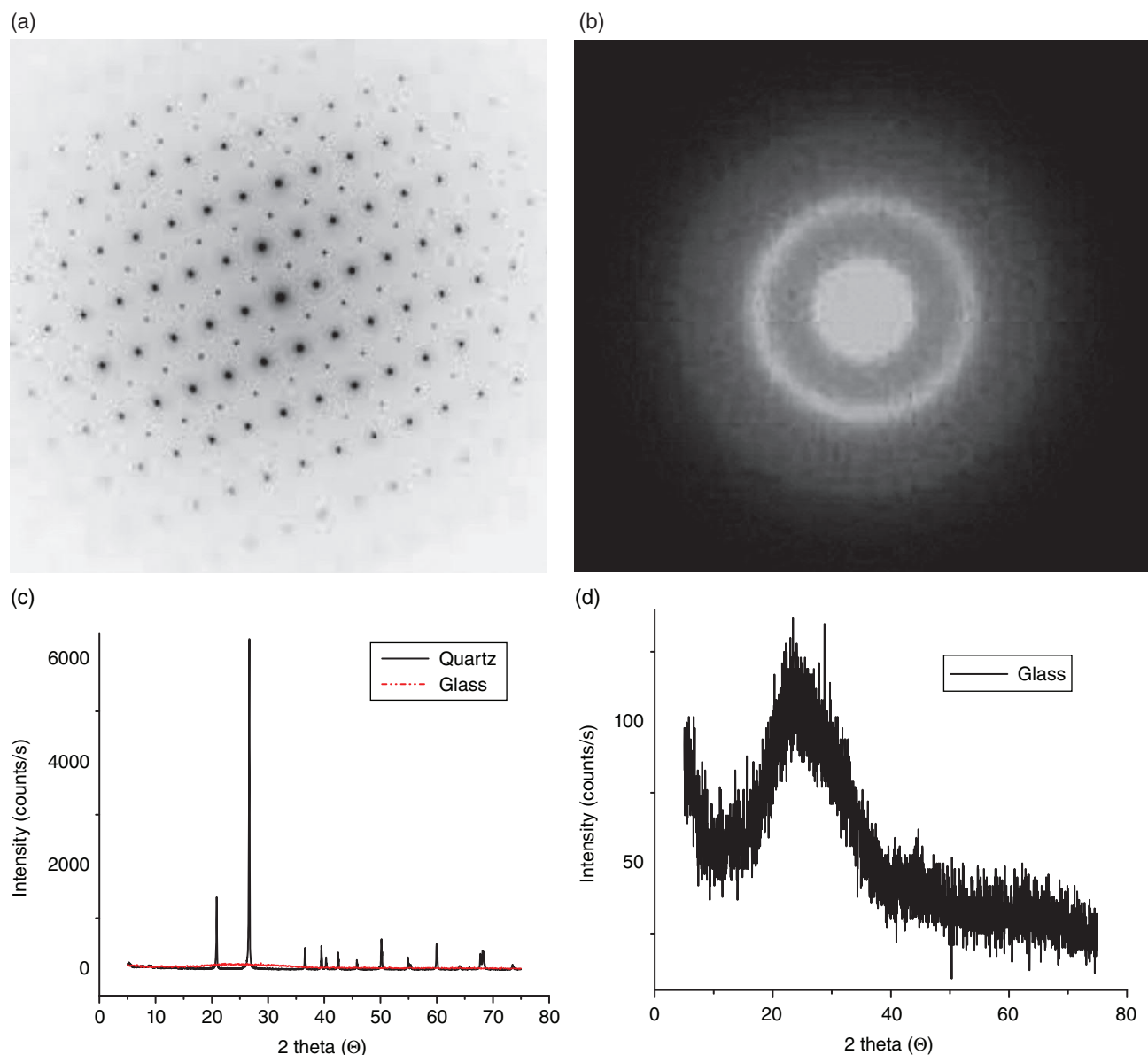


Figure 1 Structural differences between crystals and glasses revealed by diffraction images and patterns. (a) Selected area electron diffraction image of crystalline $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (fresnoite). (b) Similar image for $\text{Ba}_2\text{TiSi}_2\text{O}_8$ glass. (c, d) Powder diffraction traces for crystalline SiO_2 (quartz) and the glass slide on which the sample was mounted. Glass diffraction trace included in (c) to give an indication of the difference in intensity between a glass and a crystalline sample.

simply a series of diffuse rings or peaks reflecting those interatomic distances that prevail throughout the glass structure (Figure 1b, d). One does need to be aware that if the material is polycrystalline, it will also exhibit a series of rings but they will be better defined than those characteristic of glasses. Nevertheless, this type of diffraction image can be analyzed and interpreted to obtain average interatomic bond distances and angles, characteristic of the short-range order (SRO, nearest-neighbor distances), and to a lesser extent, the intermediate-range order (IRO). An example of SRO (typically up to ~ 3 Å) would be around a Si atom with the four oxygens of its SiO_4 tetrahedron, whereas IRO (typically up to ~ 3 – 5 Å) would be the linkage of this tetrahedron with others to form groups such as rings.

The most common information derived for glasses from the diffraction peaks shown in Figure 2 are radial distribution functions (RDF), which represent the probability of finding a given atom at any distance r from some atom considered to be at the center of the system. A RDF thus is a one-dimensional representation of the three-dimensional structure of a glass that is averaged over the entire system. Because these functions represent the sum of individual pair distributions for every atom of the material, they are widely used for comparisons with theoretical results to check the accuracy of the simulated glass structure.

If two theta (2θ) is the angle between incident and scattered beams and λ the X-ray or neutron wavelength, the wave or scattering vector is $4\pi \sin \theta / \lambda$. It is denoted as Q in

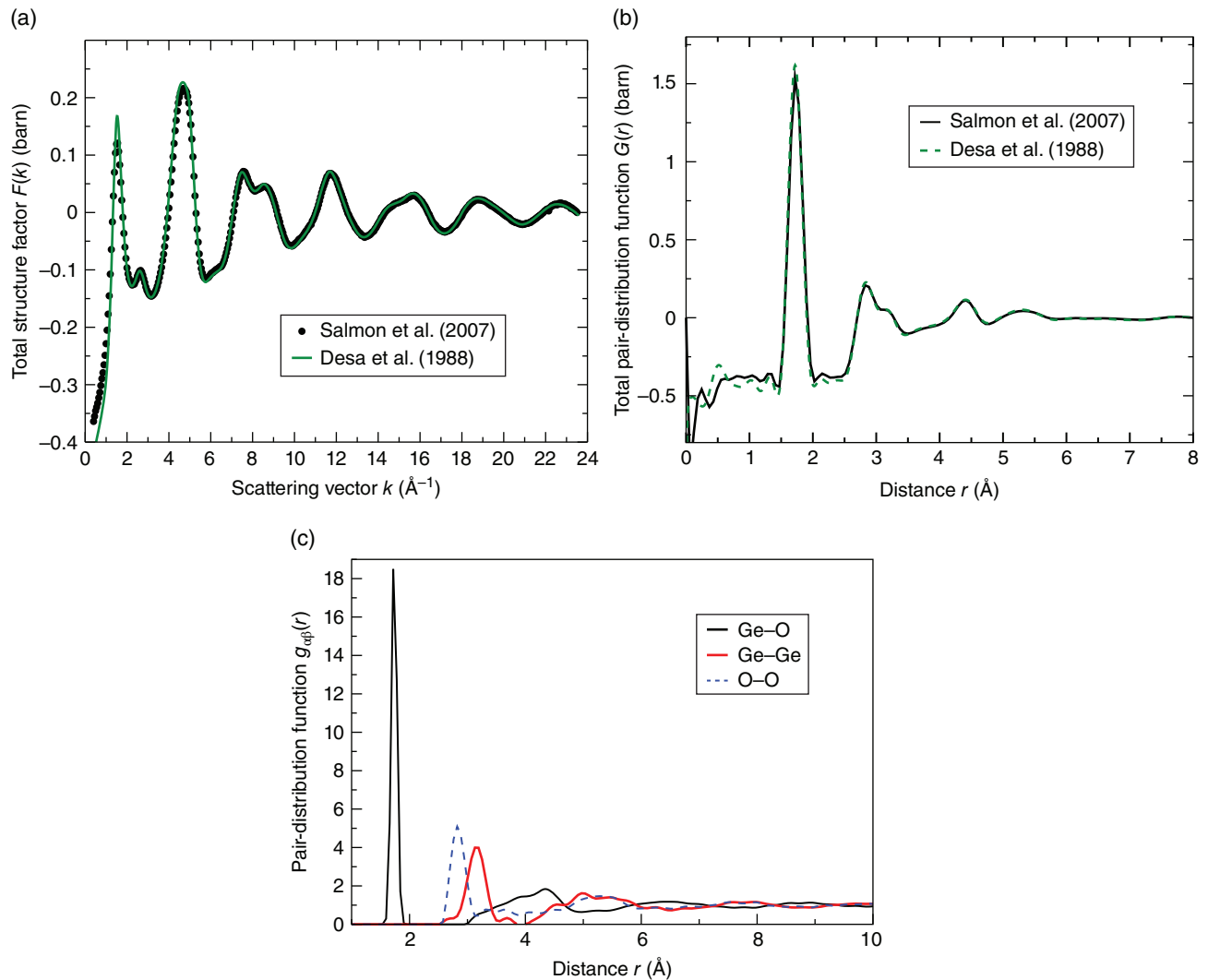


Figure 2 Information drawn for GeO_2 glass from diffraction data. (a) Measured total structure factor. (b) Total correlation function. (c) Pair-correlation functions showing the contribution from the individual atom pairs. Comparison with the earlier data of [4] is also shown. (Source: After [5].) Results corrected for a number of instrumental effects before derivation of pair distributions serving to identify the individual atomic pairs contributing to the bulk diffraction pattern of the sample.

neutron scattering, and as s or k in X-ray diffraction. In the latter case, it is common to extract the X-ray weighted Faber-Ziman or total structure factor (TSF), $S(k)$ [6], from the experimentally measured corrected coherent scattering intensity, $I_{\text{coh}}(k)$ (Figure 2a). The relationship between the TSF and $I_{\text{coh}}(k)$ is given by:

$$s(k) = 1 + \frac{I_{\text{coh}}(k) - \overline{|f|^2}}{|\overline{f}|^2}, \quad (1)$$

where $\overline{|f|^2} = \sum_i c_i f_i^2$ and $\overline{f} = \sum_i c_i f_i$. The RDF, $D(r)$, is then given by the Fourier transform of $S(k)$:

$$D(r) = \frac{2}{\pi} \int_0^\infty k [S(k) - 1] \sin(kr) dk. \quad (2)$$

The distribution function, $D(r) = 4\pi[\rho(r) - \rho_0]$, can be converted to the total pair-correlation function (Figure 2b). The TSF is the sum of the partial structure factors $S_{ij}(k)$ (PSF) for the different atoms i and j . The PSFs cause the oscillating contributions to the scattering curve and take the form:

$$S_{ij} = \frac{\sin kr_{ij}}{kr_{ij}},$$

where r_{ij} is the distance between atoms i and j . The TSF itself is expressed as:

$$S(k) = \sum_i^N \sum_j^N W_{ij} S_{ij}(k), \quad (3)$$

where $W_{ij} = c_i c_j f_i(k, E) f_j(k, E)$, C_i and C_j are the atomic fractions of species i and j , E the photon energy, and f_i and f_j the atomic scattering factors of species i and j . For GeO_2 glass, the measured TSF shows a first sharp diffraction peak (FSDP) at $1.5 \text{ \AA}^{-1}$ (Figure 2a left). From the total correlation function, i.e. the sum of all atom pair correlations (Figure 2b), one can extract (Figure 2c) partial pair-correlation functions showing the individual contributions to $G(r)$. For a binary compound such as GeO_2 , three PSFs are needed to obtain $S(k)$ (Figure 2c). These are $S_{\text{Ge-Ge}}$, $S_{\text{O-O}}$, and $S_{\text{Ge-O}}$, which correspond to contributions from Ge—Ge, O—O, and Ge—O bonds. The FSDP is characteristic of structural features in the IRO and longer length scales characteristic of long-range order (LRO). See Chapter 2.5 on the extended structure of glasses for a full discussion on the ordering ranges found in glasses.

Diffraction experiments provide information about the average structure of a glass. The positions of the peaks indicate interatomic distances, peak widths indicate bond distance variations, and the areas under the peaks are related to average CN. The RDFs have tall sharp peaks at small radial distances, but broad, low-intensity peaks at larger ones. This difference indicates that the structure is less variable at small (short-range) than at larger

(intermediate-range) radii. Consequently, the few first peaks in the correlation function can be assigned to well-defined interatomic distances whereas peaks at larger radial distance are less easily interpreted because they are composed of more than one atom pair correlation.

One can minimize the problem of overlapping contributions by collecting scattering data to higher k space to improve the resolution. One achieves this goal by using neutron scattering and collecting data out to $Q(k)$ ranges of $\sim 40\text{--}50 \text{ \AA}^{-1}$ or hard X-ray photons ($>40 \text{ keV}$) with wavelengths lower than 0.03 nm ($k \geq 30 \text{ \AA}^{-1}$). Furthermore, one can partly overcome the difficulty of interpreting peaks at high r values by using techniques that can separate the individual PSFs, such as anomalous X-ray scattering or isotope substitution. Currently, most glass diffraction experiments involve a combination of two or more techniques.

2.2 Isotope-substituted Neutron Diffraction

As already stated, this technique takes advantage of the dependence of the neutron diffraction on the number of neutrons contained in the atoms undergoing diffraction. By making isotopic substitutions in the sample, it becomes possible to eliminate some PSF in the TSF. This makes determining the various pair-correlation functions simpler and can lead to unambiguous assignment of features in the total correlation function to specific atom interactions. Basically, two experiments are performed on a sample in which one of the elements is in two different isotopic states. The two TSF can then be subtracted and their difference enables extraction of the PSF involving the element in the different isotopic states. To extract three PSF from a binary system, one requires diffraction experiments on three samples that are identical in every respect, except for the isotopic compositions of one or both of the chemical species.

The difference function is essentially similar to X-ray absorption spectroscopy (XAS) but the accuracy of the diffraction data can be improved to higher distances and providing more accurate CN of the element of interest. One should note, however, that the structural role of the two isotopes should be identical, which may not necessarily be the case as observed for light elements such as deuterium and hydrogen. The technique is similar to anomalous wide angle X-ray scattering (AWAXS) or diffraction anomalous X-ray scattering (DAXS).

2.3 DAXS and AWAXS

In these techniques, one determines the individual contributions to the TSF by each of the scattering atom pairs by using sharp changes in the X-ray scattering factor of an element near its X-ray absorption edge. The data are

qualitatively similar to those of extended X-ray absorption fine structure spectroscopy (EXAFS), but also include low- k contributions that contain information on the intermediate-range structure. Scattering data are collected at two or more different energies, one of them being close to the X-ray absorption edge of the element of interest. With AWAXS and DAXS, the idea is to cancel the correlations that do not involve the element of interest. This is also true for isotope-substituted diffraction.

3 X-ray Absorption Techniques

3.1 General Features

These atom-specific methods provide information on the structural environment of a specific element within a glass. The problem remains, however, that glasses are disordered and lack LRO so the data obtained are broadened relative to those for crystalline materials. Even though one may be looking at the structural environment of a single element, the data in addition represent the “averaged” structure over all the possible sites so that is very difficult to discriminate between distinct sites.

These methods provide similar information in spite of the different sources used for exciting the atomic interactions of interest. EXAFS or X-ray absorption fine structure spectroscopy (XAFS) along with X-ray absorption near-edge structure (XANES) spectroscopy constitute techniques that fall under XAS. EXAFS provides atom-specific quantitative data on bond distances, thermal bond-displacement parameters (i.e. Debye–Waller factors, σ), and CN. XANES can be used to determine qualitatively, the oxidation state, CN, and the electronic structure of the atom of interest. Both techniques are routinely carried out with synchrotron sources and dedicated XAS beam lines. Energy loss near-edge structure (ELNES) spectroscopy or electron energy loss spectroscopy (EELS) provides information similar to XANES, but uses instead the electron beam of a high-resolution transmission-electron microscope and relies on the energy loss as electrons are transmitted through the sample. X-ray Raman spectroscopy (XRS) or non-resonant inelastic X-ray scattering (NRIXS) is a relatively new technique that also provides similar information to XANES but uses the momentum transfer of hard X-rays (~ 10 keV) to induce the atomic interactions of interest. To date, XRS has been employed specifically to study elements *in-situ* at high pressure. Under these conditions, this is the only technique with which one can currently study elements in the soft X-ray range (< 2 keV), i.e. O, Si, Al, alkalis, and alkaline earths.

For all these techniques samples are usually powders (mgs) or glass chips (mm). For some experiments such

as transmission mode XAS experiments, however, care must be taken to ensure that the sample thickness is appropriate for the experimental conditions. If the sample is too thick, then self-absorption effects negate any useful data.

3.2 EXAFS and XANES

The closely related techniques EXAFS and XANES together constitute XAS. An XAS spectrum is divided into three regions: that of XANES, typically 0–50 eV above the X-ray absorption edge; of EXAFS or XAFS, typically ~ 50 – 1500 eV above the X-ray edge; and of the pre-edge ~ 20 – 30 eV below the edge (Figure 3). Both EXAFS and XANES are element-specific and potentially can be obtained from any element in the periodic table down to concentrations that can be as low as ~ 100 ppm.

EXAFS data are used for determining quantitatively bond distances, CN, the nature of the atoms surrounding the central atom of interest, and Debye–Waller factors. As illustrated for GeO_2 glass, the EXAFS portion of an XAS spectrum may be background corrected, normalized to 1 (Figure 4a), and then converted to k -space (reciprocal space) to get what is termed the $\chi(k)$ spectrum (Figure 4b). Part of this $\chi(k)$ spectrum is then Fourier transformed back into real space (R -space). The magnitude of the Fourier transform is essentially an RDF made up of the different atom pairs contributing to the $\chi(k)$ spectrum (Figure 4c), which is similar to the X-ray RDF. The first peak represents the Ge–O distances whereas peaks at higher R are due to multiple scattering and/or Ge–Ge, second Ge–O distances, etc. Modeling of the data (in R - or k -space) with reference to a crystalline

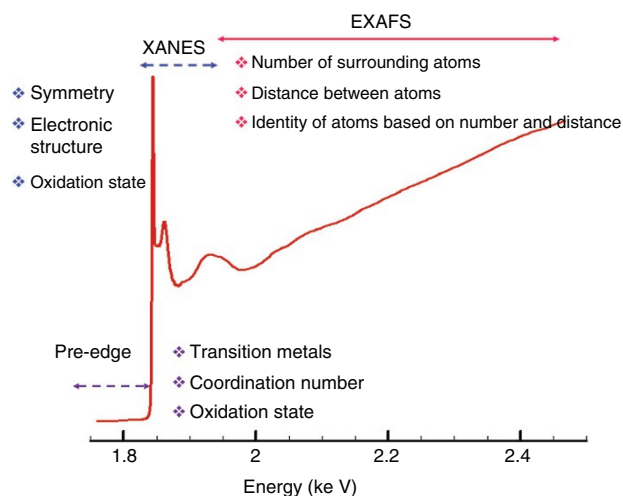


Figure 3 Typical information drawn from XAS spectra: processes causing the features observed in each energy range of interest. Spectrum of SiO_2 glass taken as an example.

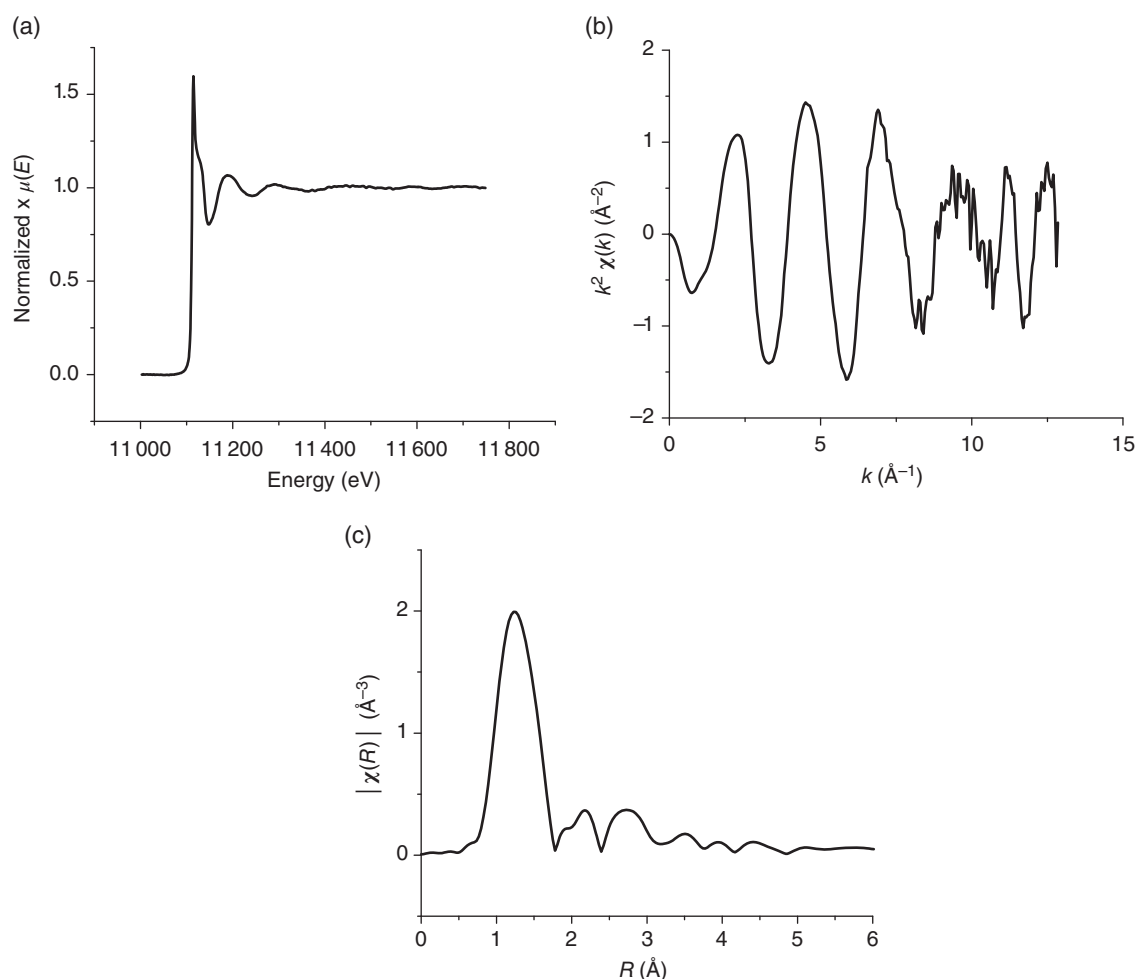


Figure 4 EXAFS portion of the XAS spectrum of GeO₂ glass. (a) Background corrected and normalized to 1. (b) Converted to k -space (reciprocal space) for derivation of the $\chi(k)$ spectrum. (c) Magnitude of the Fourier transformed $\chi(k)$ spectrum, essentially a radial distribution function made up of the different atom pairs contributing to the source $\chi(k)$ spectrum.

standard (e.g. trigonal GeO₂ in this example) is necessary to extract the real interatomic distance. Without such modeling the interatomic distances are not accurate, being generally shorter than the real ones by $\sim 0.5 \text{ \AA}$.

The information drawn from XANES (Figure 5) on the electronic structure, oxidation state, CN, and nature of the bonding within the glass is more qualitative. This limitation is illustrated by the XANES spectra of Figure 5a where fewer and broader features are observed for SiO₂ glass than for quartz. Each peak represents an electronic transition of the Si 1s electrons to 2p states mixed with unoccupied oxygen states (orbitals). Comparison of the experimental XANES with first-principles calculations greatly facilitates detailed analysis of the electronic states.

One can also use XANES to determine the relative fractions of the different phases that are present in a mixture of crystalline materials. For this purpose, it suffices to perform a linear combination analysis whereby spectra of

crystalline standards are summed together in different ratios and compared with the experimental spectrum.

Of particular interest in glass science is the oxidation state and coordination of transition metal (TM) elements. For these elements, one predominantly uses the pre-edge features of the K -edge XAS, which represent excitation of a 1s electron to a 2p state (Figure 5b). These pre-edge features arise from formerly spin-forbidden electronic transitions that become “allowed” through site distortion. For some Ti-bearing crystals, the pre-edge shown in Figure 5b may contain from 1 to 3 peaks whose intensity is highest for the second or middle peak (fourfold coordinated Ti) and decreases with increasing Ti coordination (cf. [8, 9]). For iron (Fe) there can be two to three pre-edge features whose actual number and relative intensities depend upon whether or not there is Fe²⁺ and/or Fe³⁺, as well as upon the coordination geometries fourfold (tetrahedral or square planar), fivefold (trigonal bipyramid,

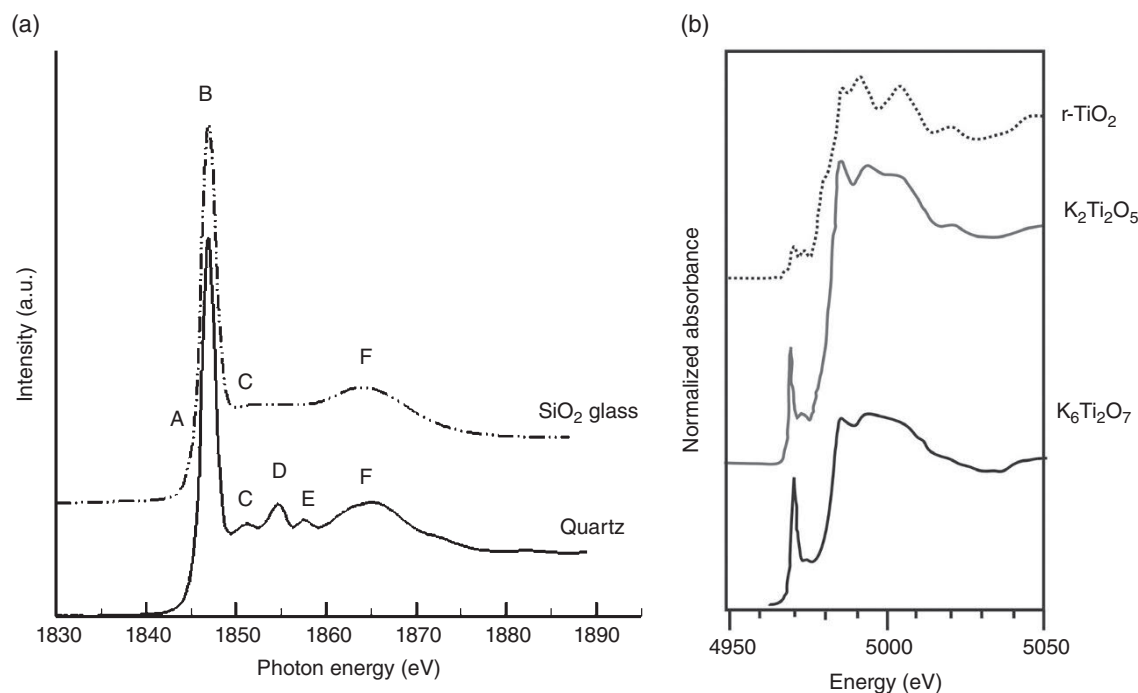


Figure 5 Information drawn from XANES data. (a) Fourfold coordination of Si in SiO_2 glass and quartz, and ordering contrast between the two phases. (b) From bottom to top, four-, five-, and sixfold coordination of Ti in crystals as derived from the pre-edge regions of Ti K spectra. Source: Reproduced with permission from [7].

square pyramid), sixfold (octahedral), or higher coordination (eightfold, etc.) of the different oxidation states.

Fits to the pre-edge features can be made to extract the positions and intensities of the different contributions. Interpretation of the data requires a comparison of both the peak positions and intensities for accurate results (see [7]). Once determined, these parameters can be used in comparison with crystalline standards to determine likely coordination and oxidation states in the glass.

In XANES experiments the L -edge of transition metals can also be used for qualitative determination of oxidation state and coordination. But this edge is inherently more difficult to interpret because it originates in excitations (of a $2p$ electron principally to $3d$ or higher states) that are affected by spin-orbit coupling of the electrons. Analysis and interpretation of both K - and L -edge XANES spectra are greatly facilitated if one has access to first-principles calculations (simulations) of the edge of interest. Provided the partial densities of states (p-DOS) are yielded by the simulations, individual peaks can be assigned to interactions between specific unoccupied states (orbitals).

In addition, the position of the edge also depends upon coordination and oxidation state, moving to higher energies with increasing oxidation, whereas the overall shape of the XANES spectrum depends on the nature of the next-nearest neighbor interactions. Consequently, one

can use a “fingerprint” technique to compare the glass XANES spectrum with those of common crystalline analogues where the element of interest is in different coordination and/or oxidation states. This approach has been widely used to estimate qualitatively CN and oxidation states.

4 Nuclear Magnetic Resonance Spectroscopy

Electrons, protons, and neutrons all have spin quantum numbers of $\frac{1}{2}$ and can therefore interact with magnetic fields externally imposed or arising from nearby particles. Nuclear magnetic resonance (NMR) occurs when NMR-active nuclei in a magnetic field absorb and re-emit electromagnetic radiation at a specific resonance frequency. This frequency depends on the strength of the magnetic field and the magnetic properties of the nuclei of interest. The sample (~ 1 – 500 mg) is perturbed while in the magnetic field by a short radiofrequency (RF) pulse (usually 90° to the applied magnetic field), which releases the energy of the resonance transition measured as a free induction decay (FID) curve in the time domain. This curve is then Fourier transformed to the frequency domain to obtain the NMR spectrum. Because the FID

is very weak, usually multiple curves are collected and time-averaged. Also of importance is the time taken for the excited spin states to return to their equilibrium distributions; the *spin lattice* (T_1) or *longitudinal magnetic* relaxation, as well as the time for the FID to reach $1/e$ of its initial amplitude, the *spin-spin* (T_2) or *transverse* relaxation. The line width of an NMR signal is determined by T_2 (a long T_2 means sharper lines) and the maximum repetition rate during acquisition of an NMR signal is governed by T_1 (short T_1 means a spectrum can be acquired in less time). Additional information about the perturbed system can be obtained when one uses multiple and often complex RF pulse sequences and investigates the time and frequency dependence of the relaxation times. The reader should see [10] and references therein for a much more detailed description of solid-state NMR.

What makes this technique important is that the measured spin energies are affected by interactions with other electrons and nuclei in the sample and, consequently, by the local chemical environment around the element of interest. Furthermore, one can also probe the dynamics of these interactions on timescales of seconds to nanoseconds that makes its application to high-temperature studies particularly useful.

Although NMR spectroscopy is used to investigate site-specific information on elements with nonzero spin quantum numbers, it is most commonly carried out for elements whose numbers are $\frac{1}{2}$ or multiples of $\frac{1}{2}$ such

as $3/2$, $5/2$, $7/2$, and $9/2$. Little information can usually be drawn from the very broad NMR spectra of solids that result from the strong anisotropy of the NMR frequencies caused by variations in electron distributions. To reduce this broadening, the sample may be spun at an angle with the applied magnetic field resulting in what is termed magic angle spinning (MAS) NMR. Although MAS does not remove all the broadening effects, one can further reduce them by using multiple quantum (MQ) MAS NMR or (MQMAS) NMR for quadrupolar nuclei (those with spin quantum numbers $> \frac{1}{2}$). Triple quantum (3Q) is most common but 5 and 7Q can also be done. In the two-dimensional spectra recorded, one dimension is the equivalent of the MAS NMR spectrum and the other is the high-resolution isotropic dimension, which is thus free of anisotropic broadening but has peak positions shifted from the isotropic chemical shift as a result of the quadrupolar broadening (cf. Figure 6). A common use of MAS NMR spectra in glass science is to discriminate the coordination environment of a number of nuclides such as four-, five-, and sixfold Al, as illustrated in Figure 6a where the existence of distinct sites are revealed in Al-bearing sodium silicate glasses quenched from high pressure (6 GPa) [10].

Other factors can also broaden the signal such as unpaired electrons, which is why NMR is of limited usefulness in the presence of transition metals or magnetic rare earth elements in glasses although progress is being made to improve the situation. On the other hand, NMR

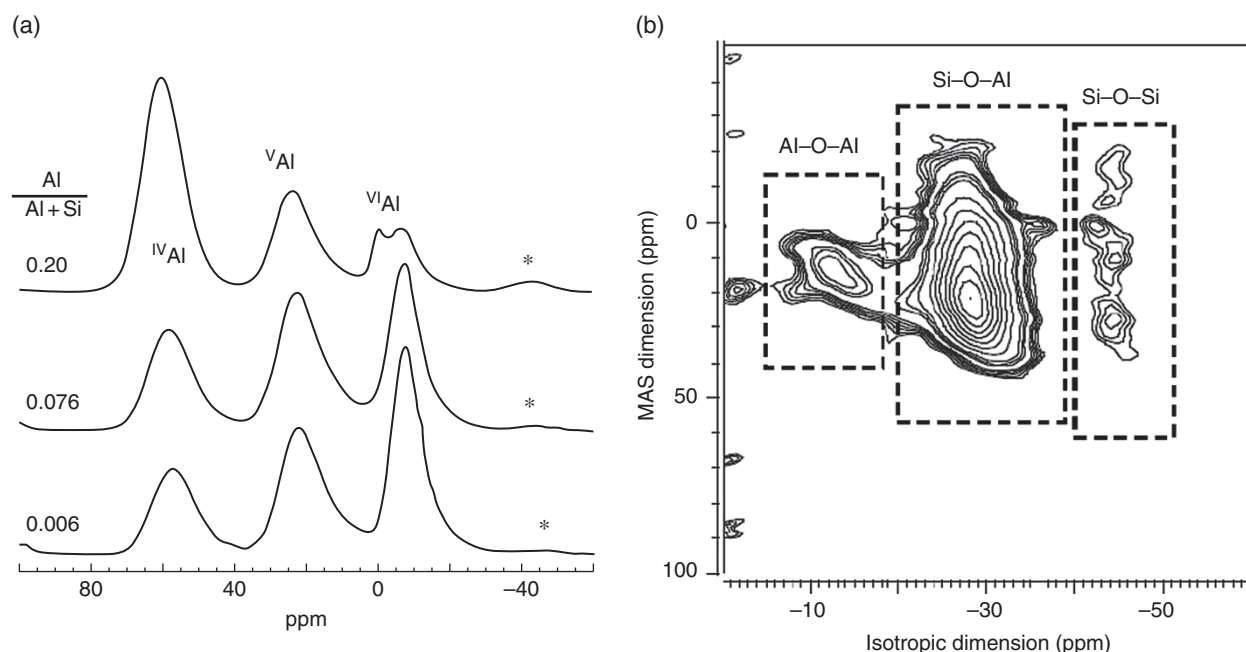


Figure 6 Structure determinations of sodium silicate glasses from ^{27}Al and ^{17}O 3Q MAS NMR spectra. (a) Aluminum coordination in samples quenches from 6 GPa. (b) Bridging oxygen linkages in the network. Source: Reproduced with permission from [10].

techniques have diversified so much in recent years to tackle such a wide variety of problems that it is impossible to summarize here these advances, or even to mention the technical terminology used by NMR experts. Rather, the reader is referred to the detailed discussion of NMR methods and applications given by Stebbins and Xue [10].

Some of the common elements studied in glasses are ^{31}P , ^{29}Si , ^{27}Al , ^{23}Na , ^{19}F , ^{11}B , ^{17}O , ^1H , and ^2H . The abundance of the NMR-active nuclide is important for determining the applicability of the technique. In some cases it is necessary to enrich the sample (usually powdered, although glass chips can also be used) with the appropriate nuclide if its natural abundance is low (e.g. ^{17}O). With appropriate nuclides, however, the sensitivity of NMR can be as low as 1% in crystalline materials and informative spectra can be collected for glasses and crystals with concentrations of the NMR nuclide well below 1%.

Typically, NMR spectroscopy provides element-specific information on short- and intermediate-range structure. The types of short-range information include coordination, Q speciation (Si tetrahedra with 1–4 bridging oxygens [BO] attached), and information on bond angles such as Si–O–Si. Intermediate-range information primarily deals with the type and nature of second neighbors, involving the connectivity of next-nearest neighbors and in some cases the connectivity of species out to fourth or higher nearest neighbors. In addition, NMR can provide dynamical information on timescales of ~ 0.1 to 1 ns and thus can investigate to some extent chemical kinetics and crystallization processes. As found with other spectroscopic techniques, NMR spectra are inherently broader for glasses than for crystals because of their intrinsically disordered nature. Double-resonance NMR methods can provide unique insights into distances between and interactions among multiple NMR-active nuclides, quite unique for NMR relative to other spectroscopies.

Spectra themselves are usually plotted as intensity versus a relative frequency scale plotted as parts per million (ppm). The frequency is reported relative to a standard and normalized by the excitation frequency:

$$\delta = 10^6 \left(\frac{\nu_{\text{sample}} - \nu_{\text{standard}}}{\nu_{\text{standard}}} \right). \quad (4)$$

The range of frequencies observed depends on the element being studied and sample composition. It is often referred to as the “chemical shift” although technically use of this term should be restricted to frequency shifts only affected by the chemical shift interaction. For ^{29}Si in glasses and minerals, it is usually in the range of -60 to -200 ppm. The chemical shift is sensitive to the coordination about the cation, higher coordinations giving rise to lower chemical shifts. Because the coordination is also strongly correlated with the cation–oxygen bond distance, the chemical shift generally decreases with

increasing bond length. At constant coordination the changes in chemical shift are much more subtle and may be partially overlapping. The chemical shifts of Q^n species (n = number of bridging oxygens) used to characterize SiO_4 tetrahedra, for instance, change by $\sim +10$ ppm with every decrease in n , and by $\sim +5$ ppm for every silicon nearest neighbor that is replaced by Al. In addition, the chemical shift depends on Si–O–Si and Si–O–Al angles, becoming more negative as the angles increase.

One of the most exciting nuclei has recently been ^{17}O NMR although the wide range of possible bonding environments for oxygen complicates interpretation of the spectra. However, ^{17}O NMR can be used to identify the cation neighbors to the non-bridging oxygens (NBOs), proportion of NBO vs BO, the coordination of the oxygens, and the nature of the cations around the NBOs. Consequently, the degree of order/disorder or mixing occurring between cations and different cation bonding environments can be resolved. For NaAlSiO_4 glass, the different BO linkages (Al–O–Al, Al–O–Si, Si–O–Si) in the network are, for instance, resolved in the ^{17}O 3QMAS NMR spectrum (Figure 6b).

5 Vibrational Spectroscopies

5.1 General Features

In the appropriate frequency ranges electromagnetic radiations can interact with the vibrational modes of a condensed phase whose energy depends on interatomic forces and on the geometry of the structural units involved. Specific structural units such as Q^n species thus have a characteristic vibrational signature whose changes as a function of chemical composition or temperature and pressure yields valuable structural information. With infrared (IR) and Raman spectroscopy, one probes in this way the interaction between atomic entities undergoing vibrational motion and an incident electromagnetic radiation whose energy is in the IR or visible regions of the spectrum. The difference between these techniques is that the interaction of the atoms and entities undergoing vibrational motion involves absorption and scattering of photons in IR spectroscopy and Raman spectroscopies, respectively, the energy of the incident photons varying by an amount (or a multiple of it) $E = h\nu = hc/\lambda$, where c is the speed of light, h Planck’s constant, ν and λ the frequency and wavelength of the vibrational mode probed. When recorded against the frequency of the light source, a spectrum thus shows a series of bands or peaks that are the fingerprints of specific vibrational modes. In contrast, Brillouin spectroscopy does not bring direct structural information because it relies on the interaction of photons with acoustic waves, which probes the bulk

and not some specific units of the substance. But it yields elastic coefficients, which themselves strongly depend on structure.

5.2 Infrared Spectroscopy

In IR spectroscopy the sample is illuminated by radiation from an IR source [11, 12]. The incident photons are absorbed if there is a change in the induced dipole moment of the bonds undergoing the vibration. This is due to the nonuniform distribution of charge along the bond. The IR radiation is measured as it is passed through (absorbed) or reflected by the sample. In general, molecules or molecular groups that have strong changes in their dipole moments (polar molecules and asymmetric vibrations) usually have strong IR spectra. Some vibrations can be observed by both IR and Raman spectroscopy whereas others may only be observed by one or the other and hence which technique is employed depends somewhat upon the types of vibrations that will be investigated.

IR spectroscopy is widely used to investigate water [13] and carbon dioxide in glasses [14], boron (B) coordination in borate glasses [15], and the structure of sol-gel derived glasses [16] and glass thin films. Kamitsos [12] has recently reviewed the application of IR spectroscopy to studies of glasses. The technique investigates the absorption or reflectance of IR radiation from the far ($\sim 10\text{--}400\text{ cm}^{-1}$) to mid-IR regions ($\sim 400\text{--}5000\text{ cm}^{-1}$). The samples can be powders (mg), glass chips (mm), or preferably glass chips where the surface of the chip has been polished. Older transmission studies often used glass powders mixed with some sort of matrix material (usually an alkali halide).

Studies on volatiles are carried out with IR absorbance techniques whereas IR reflectance methods are the most common for structural studies of glasses (especially borates) because in this case one does not need to correct for a number of spectral aberrations caused by a variety of sources such as, for example, variations in sample thickness. Reflectance spectra are transformed with the Kramers–Krönig (KK) transformation or via dispersion analysis to provide the optical and dielectric properties of the glass (cf. [12]). As in Raman spectroscopy, the observed peaks are generally characteristic of specific vibrational motions and molecular groups. In borate glasses (Figure 7) peaks at $800\text{--}1150\text{ cm}^{-1}$ are, for instance, due to B–O stretching vibrations of BO_4 tetrahedra whereas the bands at $1150\text{--}1550\text{ cm}^{-1}$ are indicative of stretching vibrations of B–O bonds in triangular borate units. The progressive changes in the $800\text{--}1550\text{ cm}^{-1}$ range observed in alkaline earth borates thus indicate a change in the B coordination from three to four when bond lengths and bond strengths change.

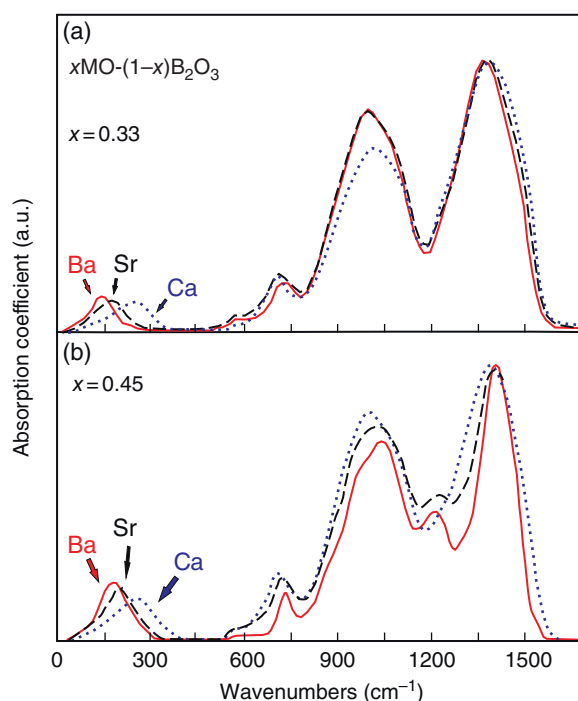


Figure 7 Band assignments in infrared absorption spectra of borate glasses obtained by Kramers–Krönig analyses of reflectance data, and effect on the absorption of the nature and concentration of (a) 33 mol % and (b) 45 mol % alkaline earth cation. *Source:* After [12].

5.3 Raman Spectroscopy

Raman spectroscopy involves illuminating the sample with monochromatic light from a laser and observation of the photons that are scattered from the sample (see [17, 18] for a comprehensive discussion). The incident laser photons interact with the molecular vibrations or phonons in the sample and some of the incident photons gain or lose energy as a consequence of the interaction. This gain or loss in energy, observed as a change in frequency of the scattered photons, is called the Raman shift and results from inelastic interactions between the incident photons and the electron cloud around the vibrating atoms in the sample. When the electron cloud is deformed, a Raman shift will occur. This deformation is termed the polarizability of the molecule or bond. The Raman shift ($\Delta\nu$) is reported in terms of cm^{-1} , where $\Delta\nu = (\nu_0 - \nu_m)$, $\lambda_0 = 1/\nu_0$ is the laser wavelength, and ν_m the frequency of the Raman band.

Raman spectroscopy is widely used to investigate the structure of glasses and amorphous materials because it is sensitive to subtle structural changes that may occur in the glass network. It can thus be used to observe a number of short- and intermediate-range features. Its primary use is in investigating changes in the connectivity

and ring statistics of the glass network and the Q^n speciation in silicate glasses.

The Raman spectrum is characteristic of the material and can be used as a spectral signature to discriminate different types of glasses, and vibrations associated with specific structural features such as small and large rings, intermediate-range structure, BO and modifier vibrations, and NBO vibrations associated with differing Q species. The relative intensity of different vibrational bands is related to the concentration and nature of the vibrational source contributing to the band and can be used to obtain the relative concentrations of different molecular groups or structural entities. In some cases it is possible to obtain quantitative information through curve fitting of the Raman spectrum, although such measurements remain somewhat controversial. The samples are usually glass chips (mm) or polished glass surfaces similar to IR.

As examples, the Raman spectrum of silica glass and a series of sodium silicate glasses are shown in Figure 8. A number of Raman bands or peaks are observed whose positions depend on the type of atoms undergoing vibration and the nature of the vibration. Their intensities depend upon the degree of polarizability of the bonds and molecular groups involved. Heavier atoms exhibit bands at lower Raman shifts because the vibrational frequency in the classic harmonic approximation depends on both the bond force constant and masses of the atoms involved as exemplified by a diatomic molecule for which $\nu = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}}$ where $\mu = \frac{m_1 m_2}{m_1 + m_2}$, c is the speed of light, f is the bond force constant, and m_1 and m_2 are the masses of the two atoms undergoing vibration.

The Raman spectrum of SiO_2 glass can be used to aid interpretation of the Raman spectra of more complex

glasses. In the $10\text{--}200\text{ cm}^{-1}$ range is the Boson peak. This peak is characteristic of glasses and its origin remains controversial; it is accepted as being related to the extended- or intermediate-range structure. Its position and intensity depend to some extent on the degree of polymerization and distortion of the tetrahedral units making up the glass network [19]. Vibrations associated with BOs generally occur in the $200\text{--}850\text{ cm}^{-1}$ region of the spectrum. In silica glass there is a strong asymmetric band at $\sim 444\text{ cm}^{-1}$, two relatively sharp bands at ~ 490 and 606 cm^{-1} , and an asymmetric band at $\sim 800\text{ cm}^{-1}$. Two weak higher-frequency bands are also observed at ~ 1080 and $\sim 1200\text{ cm}^{-1}$. Both are due to BO vibrations associated with the SiO_4 tetrahedra. More specifically they are the T_2 and A_1 modes, respectively. The former involves in-phase stretching of the BOs toward and away from the central Si, the latter out-of-phase motion of pairs of BOs: one opposed pair moves toward the Si while the other moves away from the central Si. Through curve fitting the A_1 band has also been further subdivided into two components whose assignments remain controversial. The asymmetric 444 cm^{-1} band is due to symmetric stretching or rocking of the BO associated with rings containing more than 5 tetrahedra. Its position depends on the Si—O—Si angle, the peak maximum moving to higher frequencies with decreasing angle. The sharp 490 and 606 cm^{-1} bands represent oxygen breathing modes associated with relatively planar four- and three-membered rings of SiO_4 tetrahedra. They are often referred to as the D1 and D2 defect bands and are specific to silicate glasses.

The $\sim 800\text{ cm}^{-1}$ band is actually made up of two components at ~ 802 and 840 cm^{-1} and represents what is termed a transverse optic (TO)/longitudinal optic (LO)

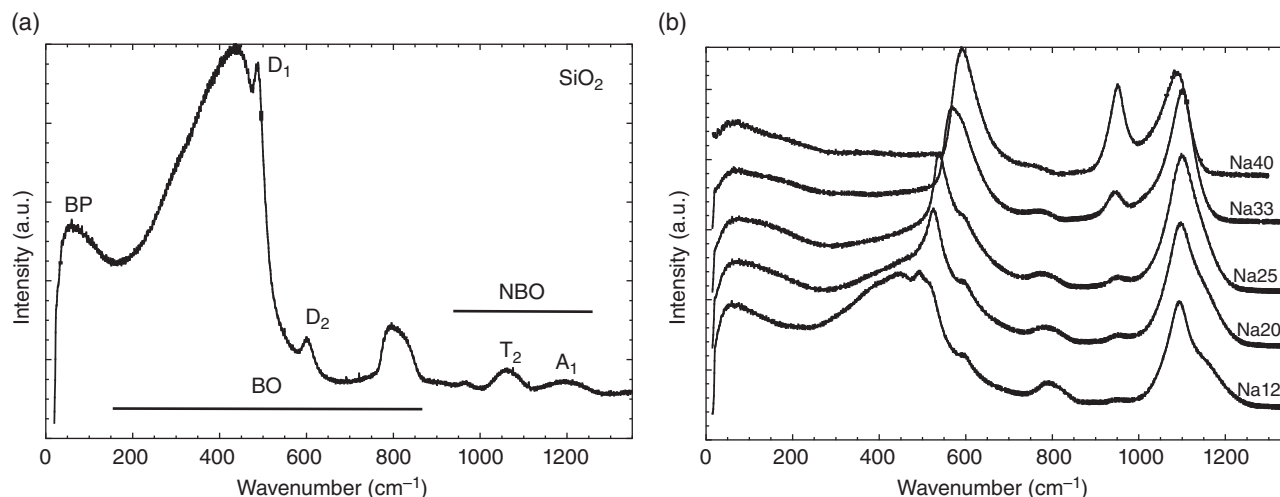


Figure 8 Band assignments in Raman spectra. (a) In the unpolarized Raman spectrum of SiO_2 glass. (b) In a series of $\text{Na}_2\text{O-SiO}_2$ glasses (12–40 mol % Na_2O added, etc.), where the different Q species are observed with increasing Na_2O content.

split band. The splitting is caused by long-range Coulombic or electromagnetic forces. These components have been variously assigned to BO bending, symmetric stretching of the BO, and various “cage” motions involving Si and/or O. When assigning any Raman band, note that it is important that care be taken in fully understanding the nature of the vibration as different authors refer to similar vibrations with different terminologies: what may be a rocking motion in one paper could be symmetric stretch in another, both referring to the same peak and relative atomic displacements.

Intense bands in the 850–1300 cm^{-1} range are generally due to NBO symmetric stretching vibrations that are generated when network modifiers are present (cf., Figure 9). Usually different bands can be assigned to different Q^n species. A summary of the Q species distribution as a function of M_2O content where M = alkalis and the Raman frequency associated with each Q species are given in Figure 9. As the number of BOs (n) increases in a Q^n species, there is a shift of the NBO vibrational band to higher wavenumbers.

Each Q species has a vibrational band that occurs in a relatively distinct frequency range although this is not always clear as these ranges may overlap and some researchers have suggested the presence of two Q^3 or two Q^2 distinct species in some silicate glass compositions [20].

With the addition of other elements such as Fe, Ti, and P, a band is often observed around 900 cm^{-1} . This band is routinely assigned to vibrations associated with the added element, i.e. $^{[4]}Fe^{3+}$ —O vibrations. However, it occurs in a variety of different composition glasses and consequently

is more likely to be a vibrational band associated with the glass network that is generated as a consequence of the added element, rather than with vibrations specifically assigned to the element itself. Nevertheless, it can be used to quantify the amount of the element added to the system (cf. [15]).

5.4 Brillouin Spectroscopy

Brillouin spectroscopy is an optical technique used to investigate the elastic properties and acoustic velocities in glasses and melts under a variety of temperature and pressure conditions (cf. [21]). The method relies on inelastic scattering of monochromatic incident photons by thermal acoustic phonon vibrations in the sample. Whereas Raman spectroscopy investigates inelastic scattering between ~ 5 and 3500 cm^{-1} from an exciting laser, Brillouin spectroscopy measures the scattered light within 10^{-2} to <10 cm^{-1} (usually ± 1 – 2 cm^{-1}) of the laser line with a resolution of 10^{-3} cm^{-1} . Measurements can be made with two different kinds of sample geometries. With the so-called platelet geometry, the incident and scattered beams make the same angle θ with the normal to the in and out surfaces. One then derives the sound velocity from the relation

$$v_{s,p} = \frac{\lambda c \Delta\sigma}{2 \sin(\theta/2)}, \quad (5)$$

where $v_{s,p}$ is the sound velocity; λ and c the wavelength and velocity of light, respectively; $\Delta\sigma$ the observed Brillouin shift; and θ the angle between incident and the scattered light. Experiments made with the backscattering geometry are simpler to perform as they require only a polished surface, but the index of refraction then needs to be known independently to determine the elastic properties.

The spectra consist of peak doublets on either side of the laser line frequency. The position, intensity, full width at half maximum (FWHM), and polarization of the peaks give information on the acoustic velocities and viscoelastic properties, coupling coefficients (between fluctuations and the electromagnetic field), the lifetime of the interactions and the anisotropy of the interaction, respectively. Thus, one can use changes in acoustic velocities, for example, to infer the occurrence of polymorphism/polymorphism at high pressures in glasses such as SiO_2 (e.g. [22]). Figure 10 shows a number of spectra for an anorthite composition ($\text{CaAl}_2\text{Si}_2\text{O}_8$) glass at various pressures. Note the structural change between 5.4 and 7.2 GPa (*indicates peaks due to the pressure transmitting medium) indicated by the shift in the peak at $\sim \pm 40$ GHz. The elastic line region is the exciting laser line and notch filter cutoff.

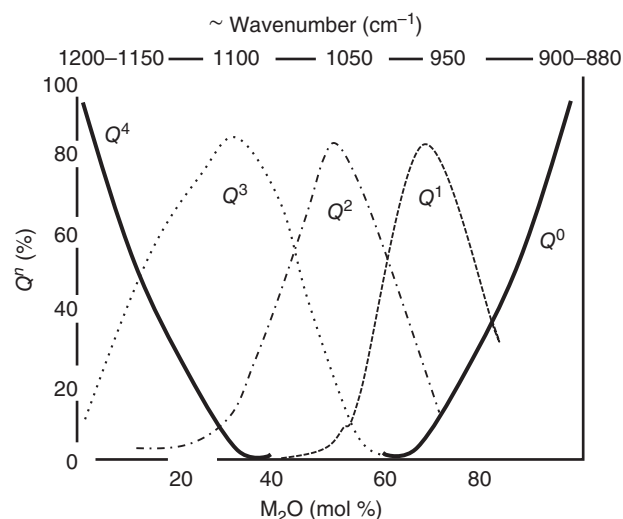
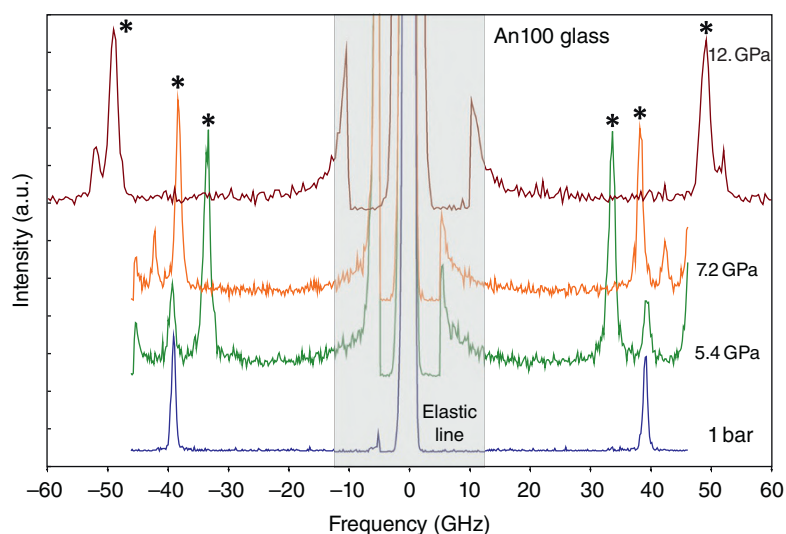


Figure 9 Raman signatures of the different Q species in alkali-containing silicate glasses. Source: Reproduced with permission from [18].

Figure 10 Evolution of Brillouin spectra with the pressures from which an anorthite glass ($\text{CaAl}_2\text{Si}_2\text{O}_8$) was quenched.



6 Other Techniques

In addition to the common methods discussed above (Sections 2.1–5.4), a number of other techniques can be used to probe more specific structural features.

6.1 Mössbauer Spectroscopy

This extremely sensitive technique relies on the recoil-free resonant absorption and emission of gamma rays in solids (Mössbauer effect). It probes small changes in energy levels associated with the nucleus. However, only a relatively limited number of elements are suitable for study. This is because Mössbauer spectroscopy relies on the radioactive decay of a parent isotope to that of interest, which has a sufficiently long half-life to make real-time experiments realistic. In glasses, the most common elements exhibiting this effect are iron (^{57}Fe) and tin (^{119}Sn), the radioactive sources being ^{57}Co and usually $^{119\text{m}}\text{Sn}$, respectively (cf. [23]). The samples are usually powders (mg) that are mixed with some sort of inert matrix such as sucrose in order to dilute the concentration of the Fe or Sn. If the Fe or Sn concentration is too high, a useful Mössbauer spectrum will not be obtained. One can determine the oxidation state and coordination of Fe in glasses based on the analysis of the isomer shift (IS) and quadrupole splitting (QS) values extracted from Fe Mössbauer spectra. The spectra of iron-containing glasses generally exhibit an asymmetric doublet whose full width at half maximum are larger than those of crystalline materials. A number of different models are usually fitted to the doublet (Figure 11). In early studies sets of symmetric Lorentzian curves were used to represent the different potential Fe sites but in more recent years fits of the quadrupolar splitting or hyperfine

field distributions are usually preferred. Typical IS (δ) values for silicate glasses fall between 0.20 and 0.32 mm/s for Fe^{3+} in tetrahedral coordination, 0.35–0.55 mm/s for Fe^{3+} in octahedral coordination, 0.80–0.95 mm/s for Fe^{2+} in tetrahedral coordination, and 1.05–1.55 mm/s for Fe^{2+} in octahedral coordination. The presence of fivefold Fe has been observed in glasses with IS and QS values lying between those of four- and sixfold Fe. However, it is difficult to distinguish Fe in fivefold coordination from a mixture of Fe in four- and sixfold coordination.

Tin spectra are usually broad (FWHM ~ 1 mm/s) symmetric doublets. For Sn^{4+} , QS values are small and the IS is close to 0 mm/s whereas Sn^{2+} has IS and QS values of 1–2 and 2–3 mm/s, respectively. For Sn^{2+} , the IS is more negative for tetrahedral than for octahedral sites.

6.2 X-ray Photoelectron Spectroscopy

Although it has been widely used to study the surfaces of materials (see [24]), X-ray photoelectron spectroscopy (XPS) can also provide information on the bulk structure. Its application to glasses has been relatively limited to date but it can determine quantitatively the NBO and BO concentrations as well as the concentration of free oxygen (O^{2-}), the oxygens not bound to a network former. The technique measures the kinetic energy of photoelectrons that are ejected from the sample (a mm-glass chip with a freshly exposed surface) as a result of ionization of an element by an incident X-ray beam. The kinetic energy of the photoelectron can be simply related to the binding energy (BE) of the electron to the nucleus so that it is characteristic of both the element from which it has been ejected and the environment around the element. One can scan for the

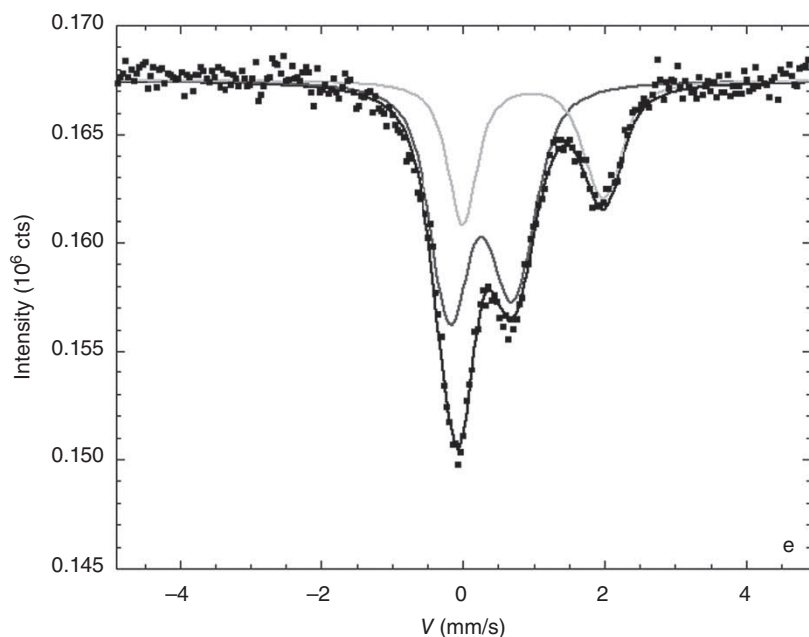


Figure 11 Contributions of Fe^{2+} (light gray) and Fe^{3+} (dark gray) to the Mössbauer spectrum of a Fe-containing borosilicate glass as determined from fits made with 2-d Gaussian distributions [15].

presence of specific elements and obtain high-resolution spectra of well-resolved energy ranges. The concentration of the different oxygen species are determined by curve fitting of the O 1s XPS spectrum [25]. The BO BE is at higher energy ($\Delta \sim 1.4$ eV) than the NBO peak but their FWHM are comparable (average ~ 1.22 eV). The free oxygen peak is incorporated into that of the NBO to the low-energy side and is observed as an increase in the FWHM of the NBO peak. This is shown in Figure 12 for a PbO-SiO_2 glass. The NBO peak has two contributions, one from the NBOs and one from the presence of free oxygen (O^{2-}), also called non-network oxygen.

6.3 Ultra Violet/Visible Spectroscopy

The absorption, reflection, or emission of light in the near UV to near IR ($\sim 250\text{--}3000$ nm) is also a source of structural information. In UV/Vis spectroscopy, one thus measures the absorption of light by a material caused by a number of factors: electronic transitions of transition metal d electrons, intervalence charge transfer (IVCT) and anion–cation charge transfer, electronic transitions between the conduction and valence bands, vibrational overtones, electronic transitions between f-orbitals, defects, and electron holes [26]. The technique is primarily used to investigate the causes of color in glasses through the oxidation and coordination environment of coloring transition metal elements such as Ni within glasses (Chapter 6.2). In general, specific absorption bands are observed that are characteristic of the transition metal, its oxidation state, and coordination. The

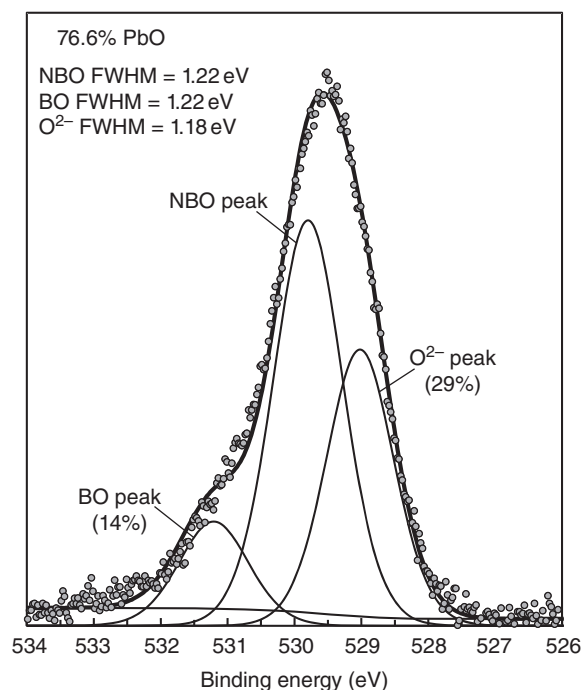


Figure 12 The different oxygen species identified from the XPS O 1s spectrum of a lead silicate glass. BO peak is constrained to a linewidth of 1.22 eV and fitted with two peaks in the NBO envelope, one due to NBOs and the other to the presence of free oxygen. Glass made and spectrum obtained by Ryan Sawyer, University Western Ontario.

samples are usually polished glass chips (mm) or slabs (mm–cm). In addition, sample thickness may need to be adjusted for specific experimental conditions.

7 Perspectives

In this chapter I have by no means covered all the possible methods that can be used to investigate the structure of glasses. In addition to variations in many of the specific techniques covered in this chapter, many more techniques including imaging methods such as atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) can be used (Chapter 2.3). Whereas the ability to “solve” the structure as done in crystal-structure analysis is not possible, our ability to probe the structure of glasses has greatly improved since the first studies in the early decades of the twentieth century. Progress in X-ray and neutron sources, lasers, detector sensitivity and resolution, and computers have all contributed to improve greatly the resolution and length scales observable in glasses and other amorphous materials.

Unlike for crystalline materials, however, any structural study of a glass must involve a multi-technique approach since no single method can supply information on all aspects of the structure. In addition, it is advantageous to use numerical techniques such as simulations of spectra, first-principles molecular dynamics (MD) simulations, and reverse Monte Carlo (RMC) calculations to aid interpretation of the experimental data. While our understanding of the SRO continues to improve, that of the IRO and LRO remains murky, as is the link between structure and, physical properties and behavior, as well as, structural changes that occur with increasing pressure and temperature. With continued advances in experimental instrumentation and computational methodologies, the outlook for resolving many of these structural issues is good.

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2.3

Microstructure Analysis of Glasses and Glass Ceramics

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1 Introduction

A homogeneous glass by definition lacks a microstructure at a scale larger than a few nanometers. As soon as actual inhomogeneities occur, in contrast, a detailed picture of their size, distribution, composition, and spatial arrangement becomes important to understand the properties of the material. In turn, the improved capabilities of microstructural studies in terms of spatial and elemental resolution are becoming increasingly important to optimize crystallization or phase separation and to achieve the desired microstructure and associated properties (Chapter 7.11). As a matter of fact, the beauty and challenge of glasses and glass ceramics is their diversity and complexity.

The purpose of this chapter thus is to review the main microstructural methods commonly used to study inhomogeneous glass-based materials. In preamble, however, it is important to note that studying extremely small volumes in great detail can result in “knowing everything about nothing.” In other words, it is critically important to make sure that the information gathered locally is actually representative for larger volumes. To achieve this goal, highly resolved information must be combined with additional integral measurements to get a broad picture. In addition, artifacts introduced upon either preparation or investigation of the sample must be avoided. And one should also be extremely careful with *in situ* microstructural experiments where, because of dramatic differences in the surface-to-volume ratio, annealing can easily lead to results not observed in the bulk. For this reason, one is advised to freeze a microstructure evolution by stopping

it at specific steps and to use multiple samples taken from different stages for gaining a “full-picture” characterization.

When dealing with the early stages of crystallization or nanoscale phase separation, it is obvious that light microscopy is not an appropriate analysis technique because its optical resolution of a few 100 nm, which is limited by the wavelengths of visible light, is two orders of magnitude too low. Fortunately, however, there are various ways to improve spatial resolution. As described in Chapter 2.2, the first is to probe the material with photons of shorter wavelengths such as X-rays: at 154 pm, the wavelength of Cu- K_α X-rays is for instance 1000 times shorter than that of visible light. A second way is to take advantage of the wave-particle dualism of electrons or ions. Under accelerating voltages of 25 and 200 kV, the electron wavelengths are even shorter than that of typical X-rays, with values of 8 and 2.5 pm, respectively. As a matter of fact, the former value is typical for studies of sample surfaces by scanning electron microscopy (SEM), whereas the latter applies to investigations by transmission electron microscopy (TEM) of bulk samples with a thickness of a few tens of nanometers at most, to limit electron absorption. In addition to these two techniques, to which we will pay particular attention, the third way to achieve high resolution will also be described. It relies on the use of scanning probes whereby a needle that is atomically sharp at its end is moved over the sample surface by a piezo drive that must be highly precise, since the key to resolution is, in this case, the accuracy of the needle position.

In practice, the formation of a given microstructure can be extremely complicated, including secondary, ternary, or even quaternary phase separation or the nucleation of multiple functional phases on finely dispersed seed crystals [1, 2]. Rather than trying to document all such processes, we prefer to illustrate the capabilities and complementarity of the methods described in this chapter

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with a single glass ceramics whose starting composition (in mol %) is $50.6 \text{ SiO}_2 \cdot 20.7 \text{ MgO} \cdot 20.7 \text{ Al}_2\text{O}_3 \cdot 5.6 \text{ ZrO}_2 \cdot 2.5 \text{ Y}_2\text{O}_3$, whence its MAS acronym from its main components MgO , Al_2O_3 , and SiO_2 . Under an appropriate temperature and time treatment, this glass transforms to a glass ceramics whose microstructure shows a variety of features with which the pros and cons of the most common techniques are nicely illustrated [3–17]. And this glass ceramics also illustrates how a specific material property can be explained only in microstructural terms: in this instance an unusually high bending strength exemplifies differential expansion strengthening (Chapter 3.12) resulting from precipitation of ZrO_2 (zirconia) and MgAl_2O_4 (spinel), two crystals with high thermal expansion coefficients, in a glassy matrix of lower expansivity.

Acronyms

AFM	atomic force microscopy
BSE	backscattered electron(s)
CL	cathodoluminescence
EDXS	energy-dispersive X-ray spectroscopy
EELS	electron energy loss spectroscopy
FIB	focused ion beam
HAADF	high-angle annular dark field (imaging)
MAS	magnesium aluminosilicate (glass ceramics)
SAED	selected area electron diffraction
SE	secondary electron(s)
SEM	scanning electron microscopy
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
XRM	X-ray microscopy
WDXS	wavelength-dispersive X-ray spectroscopy

2 Scanning Electron Microscopy

2.1 Image Formation

In SEM a finely focused primary electron beam possessing an energy in the 100 eV–30 keV range impinges onto the surface of a sample placed in vacuum (Figure 1). By interacting with the sample atoms, electrons generate many different signals. If the primary electron beam is scanned across the surface, an image can be formed not only from secondary electrons (SE) but also from backscattered primary electrons (BSE) and cathodoluminescence (CL). In addition, the chemical composition of the sample surface can be determined from the generated X-rays and Auger electrons.

The primary beam diameter can be as small as a few nanometers, but the magnification is determined by the distance between the positions of the beam successively held to acquire one of the secondary signals and to generate an intensity signal in the digital image derived. Well below the sample surface exposed to the scanning electron beam, however, even the smallest primary beam undergoes some scattering upon interaction with the atoms in the bulk of the sample. Channeling effects may also occur if the sample is fully or partly crystalline, i.e. electrons may penetrate more deeply into some areas of the sample before scattering if a specific crystallographic orientation is well aligned with the direction of the electron beam. The spatial resolution of an SEM micrograph is, therefore, rather determined by the interaction volume (with typical extensions of several 100 nm in width and depth beneath the surface; cf. Figure 1) than by the initial spot size of the beam.

Depending on the type of (secondary) signal used for imaging and analyzing the sample, the depth of information and, accordingly, the lateral resolution as well will be very different. For instance, SE have energies lower than

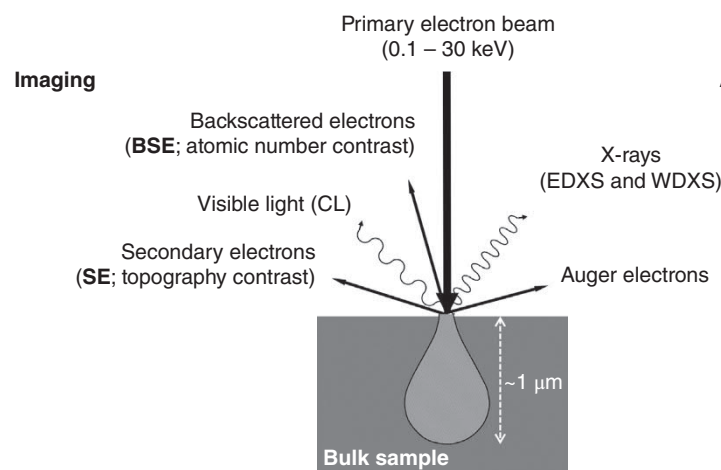


Figure 1 Interaction volume and main secondary signals occurring when a primary electron impinges on a sample surface.

about 50 eV. Those that leave the sample surface can thus reach the detector system only if they stem from the “neck” of the excitation volume, i.e. down to approximately 50 nm beneath the surface. The SE generated at greater depths do not reach the surface to leave the sample because of self-absorption effects resulting from their rather low energy. On the contrary, the highly energetic backscattered electrons (BSE) – as well as the X-rays used for chemical analysis – may also stem from the “bulk” of the excitation volume, further below the sample surface down to some 100 nm. This interaction volume strongly depends on experimental factors that can be adjusted to some extent. For instance, reducing the acceleration voltage reduces the sample penetration depth and, thus, the size of the resolution-determining excitation volume. It may also help to increase the resolution by reduction of sample charging, a problem that is always encountered when nonconducting samples (like most glasses) are analyzed.

Such adjustments, however, might worsen other aspects of the experiment. When probing the sample composition from the energy of the characteristic X-rays emitted, the primary electron beam should, for instance, have an energy that is high enough to generate these X-rays. In other words, an acceleration voltage amounting at least to twice the X-ray energy to be excited is needed, in spite of its ensuing implications on interaction volume, charging, and also sample degradation. In summary, one should always think first about the intended experiment – the crucial information to be gained – and adjust the experimental conditions accordingly.

An advantage of SEM is that sample preparation is simple. Glasses and glass ceramics are typically just ground and polished. More specific techniques rely on wet-chemical etching to generate a topography related to the differing dissolution rates of the constituents of the microstructure (e.g. the vitreous “matrix” vs. crystalline precipitates) and on focused ion beam (FIB) etching to get access to regions buried under the surface.

When glasses are electric insulators, care must be taken to avoid accumulation of electrical charges on the surface, which could influence image formation by deflecting ingoing or outgoing electrons, particularly those that possess only low energies. Coating the sample with a few nanometers of carbon helps drain away such charges, but potentially covers fine details of the microstructure and adds a local source of contamination by carbon redistribution on the surface. Another way to prevent charging is imaging under poor vacuum conditions. This is done in so-called environmental or vapor-pressure SEMs, where a certain partial pressure of, for example, water vapor is maintained above the sample surface, whereas a pressure gradient ensures that the electron-emitting source is kept in ultrahigh vacuum. In this experimental setup, primary

electrons ionize water molecules that eventually neutralize charges on the sample surface. Last but not least, the total electron yield (SE and BSE leaving the sample) depends on the acceleration voltage. Provided that this voltage can be properly varied, conditions can be found such that as many electrons enter the sample as leave it, resulting in the absence of charging. Typically, such conditions are encountered for acceleration voltages of only a few 100 V. Whereas imaging resolution is improved in this way, the disadvantages include an enhanced susceptibility toward contamination of the scan field as well as a practical inability to perform X-ray spectrometry because the electron energy will be insufficient to induce X-ray emission from the sample.

2.2 Chemical Analyses

Characteristic X-rays excited by high-energy electrons can be recorded either by energy-dispersive X-ray spectroscopy (EDXS) or by wavelength-dispersive X-ray spectroscopy (WDXS). Stemming from electronic recombination, the X-rays generated fingerprint the electronic structure of the excited element, thus making quantitative analyses possible. Soft X-rays (e.g. emitted by light elements) are subject to absorption on their way out of the sample, however, so with decreasing atomic number, the emission of Auger electrons counteracts that of X-rays. Hence, quantification for elements with atomic numbers smaller than 13 requires extraordinary diligence.

In EDXS, a semiconductor detector is used to count electron-hole pairs generated by the impinging X-rays. The spectral resolution is typically on the order of 130 eV, so in a few cases overlapping emission lines cannot be clearly separated: this will, for instance, apply to the $\text{Ti } K_{\alpha 1}$ and $\text{Ba } L_{\alpha 1}$ at about 4.51 and 4.47 keV, respectively. This problem is less serious with WDXS (with a spectral resolution of ≈ 10 eV), where Bragg’s law of selective reflection forms the basis of detection in a proportional counter. Whereas EDXS is a parallel-registering technique, WDXS (which is very similar to electron microprobe analysis [EMPA]) is a serial technique, making it more time consuming and less commonly used than EDXS.

For a sufficient yield of X-rays of a certain energy, as a rule of thumb, the primary electrons should have a kinetic energy of at least twice that amount. As an example, $\text{Si-}K_{\alpha}$ X-rays possess an energy of 1.74 keV, which is similar to the difference between the $\text{Si-}K$ and the $\text{Si-}L_{2,3}$ energy levels in the electron shell of the Si atom. Thus, one needs to use at least 3.5 kV acceleration voltage to be able to detect Si in a glassy sample by means of EDXS or WDXS, let alone any heavier elements. Low-voltage excitation in

SEM might thus be advisable for imaging purposes, but not for chemical analysis.

2.3 Application to Glass Ceramics

To illustrate the information depth one can gain with that technique, the aforementioned MAS glass ceramics will be selected. In this sample, precipitation of zirconia and spinel is known from X-ray diffraction (XRD) experiments, but this technique is inappropriate for investigating the micro- and nanostructure because it gives information about the sample as a whole, with a low spatial resolution defined by the X-ray spot size. Techniques such as SEM or TEM must be used instead, and they can in addition yield the composition of the residual glass and the structure of the crystals – in this case whether zirconia is the tetragonal, cubic, or monoclinic polymorph.

For a piece of this MAS sample, polished and rendered conductive by deposition of a $\approx 3\text{--}5\text{ nm}$ carbon film on its surface, an SEM micrograph (SE) taken with an acceleration voltage of 10 kV clearly shows bright, elongated

structures and areas with brighter and darker appearance (Figure 2a). A comparison with an SEM micrograph acquired at a 30 kV acceleration voltage (Figure 2b) illustrates the loss of both resolution and contrast when the energy of the primary electrons increases and results in deeper electron penetration in the bulk. In turn, the effect makes the origin of the image-forming SE less predictable, so fine details are smeared out at the surface of the sample. At a higher magnification (Figure 2c), the microstructure observed with a 10 kV acceleration voltage from backscattered primary electrons (BSE) shows the dendritic appearance of the brightest, elongated features that indicate their crystalline nature. Resulting from strong scattering of the primary electrons, the marked contrast of these features with their surrounding suggests the presence of heavy elements (and associated high backscattering yield). Given that zirconia is present in the sample and that the other heavy element besides zirconium, i.e. Y, is not expected to enter another crystalline phase in this material, one can conclude that the bright dendritic microstructure is likely made up of zirconia.

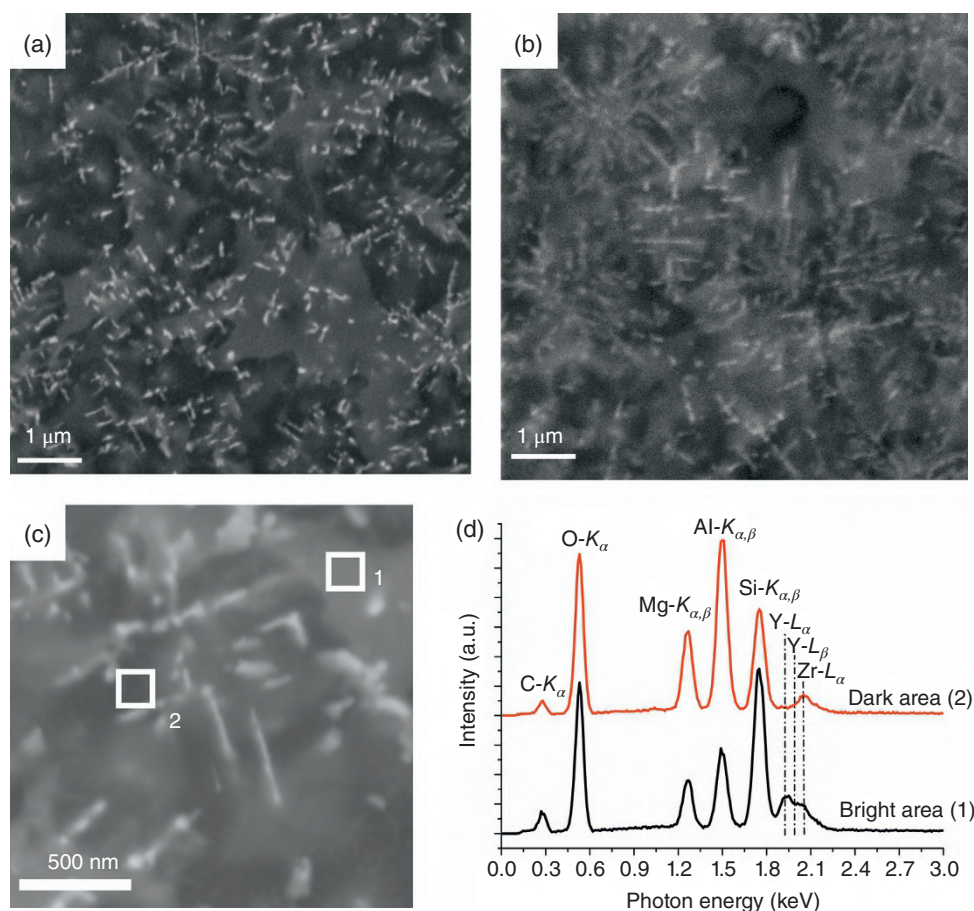


Figure 2 Scanning electron micrographs of the MAS glass-ceramic sample: resolution differences between 10 kV (a) and 30 kV (b) acceleration voltages and BSE micrograph taken at 10 kV at higher magnification (c) showing the bright (1) and dark (2) areas for which the EDX spectra of (d) were acquired.

Around the dendrites, the brighter and darker areas should then be the images of the spinel and the residual glass, respectively.

To check this conclusion, EDXS analyses were made in the two areas indicated in Figure 2c. The spectra are presented in Figure 2d. In both, a small carbon peak is an artifact of the sample preparation. Besides the most intense oxygen and silicon peaks, the other peaks are readily assigned to the other elements, but a clear separation of the $Y-L_{\beta}$ and $Zr-L_{\alpha}$ peaks is not possible owing to the limited energy resolution of the EDX detector system. The better separated $Y-K$ (at ≈ 14.9 keV) and $Zr-K$ lines (at ≈ 15.7 keV) would be more suitable, but a higher acceleration voltage would be needed to access that higher-energy part of the EDX spectrum with its ensuing loss of image resolution.

Nevertheless, these EDX spectra suggest that the brighter areas likely are silica rich, most probably depicting the residual Y-bearing glass. Conversely, the darker areas should consist of spinel, which is Si- and Y-free, as confirmed by analyses made in the “darker” area of the sample where O, Al, and Mg are found with a higher Al/Si ratio than in the other spectrum. The reason why certain amounts of Si and also of Zr (but not of Y) are nonetheless detected is that a certain interaction volume is also excited below the surface within the sample (cf. Figure 1). As a result, the lateral resolution is worsened, and the probed area does not include only the “dark” region 1 that is visible in Figure 2c, yet also parts of the sample bulk below. In conclusion, like any technique, SEM and EDXS have their own limitations. Other methods having a higher resolving power must be used to overcome them.

3 Transmission Electron Microscopy

3.1 Conventional Observations

Analytical (scanning) transmission electron microscopy [(S)TEM], currently is the best method for both imaging and determining chemical compositions [18] whenever the relatively large excitation volume of SEM becomes problematic. The price to be paid is the necessity to prepare samples as thin as a few 10 nm, without preparation artifacts, to make them transparent to electrons. The task is difficult, but over the years a wide range of techniques have been developed for this purpose, including mechanical grinding, ion beam etching, preparation of replica, ultramicrotomy, and FIB machining of lift-out TEM lamellae [19]. In this respect one should distinguish between samples taken from the bulk and cross-sectional samples cut out from specifically targeted areas (e.g. if a specific source of devitrification in a glass has to be

assessed for further analysis) for which FIB machining is particularly well suited.

In its principle, a transmission electron microscope is amazingly similar to a light microscope: the electron source corresponds to the lamp; beams are formed by electromagnetic lenses (which are true zoom lenses as one can finely change their focal length by altering the lens current); image and object planes are defined; and after converting the electron distribution into light with a scintillator, an image is formed and registered by a CCD or CMOS camera. Of course, however, TEM offers a number of tremendous advantages over light microscopy that result from the much lower wavelengths of electrons compared with those of visible light. First and foremost, it has a much higher spatial resolution, as the best commercially available instruments can now resolve lattice planes as close as 50 pm apart [20]. Second, unlike for optical lenses, the focal lengths of electron lenses can be changed during operation, allowing for switching between parallel illumination and formation of a focus spot of less than 100 pm in diameter for dedicated analyses of very small sample regions. Third, one can switch between imaging and diffraction modes, which makes it possible to identify crystalline phases from the recorded electron diffraction patterns. Fourth, the higher energy of electrons (as compared with visible light) allows electronic transitions to be excited, laying the ground not only for analyzing chemical compositions (EDXS) but also for assessing the coordination and valence of appropriate elements (electron energy loss spectroscopy [EELS] [21]).

In conventional TEM, the sample is illuminated with a parallel beam. Bright- or dark-field micrographs are recorded depending on whether or not one includes in the image formed the primary (central) beam in the diffraction plane, which is the back focal plane (Figure 3). Contrast, i.e. the visibility of objects, in bright-field imaging is simply explained: if a certain area scatters (inelastically) or diffracts (elastically) more strongly than its surroundings, the electrons passing through this area will be deflected to higher angles than the non-scattered or less scattered/diffracted electrons. By introducing a contrast aperture (the objective aperture in Figure 3), one blocks electrons traveling far from the optical axis. As a consequence, the corresponding areas in the micrograph appear less bright.

For glasses and glass ceramics, microstructures typically generate various kinds of contrasts. In liquid–liquid phase separation, droplets containing elements heavier than those of the surrounding matrix appear as less bright regions on micrographs (although atomic number differences can be so small as to make phase-separated droplets hardly discernable). Crystalline precipitates always appear much darker than their glassy

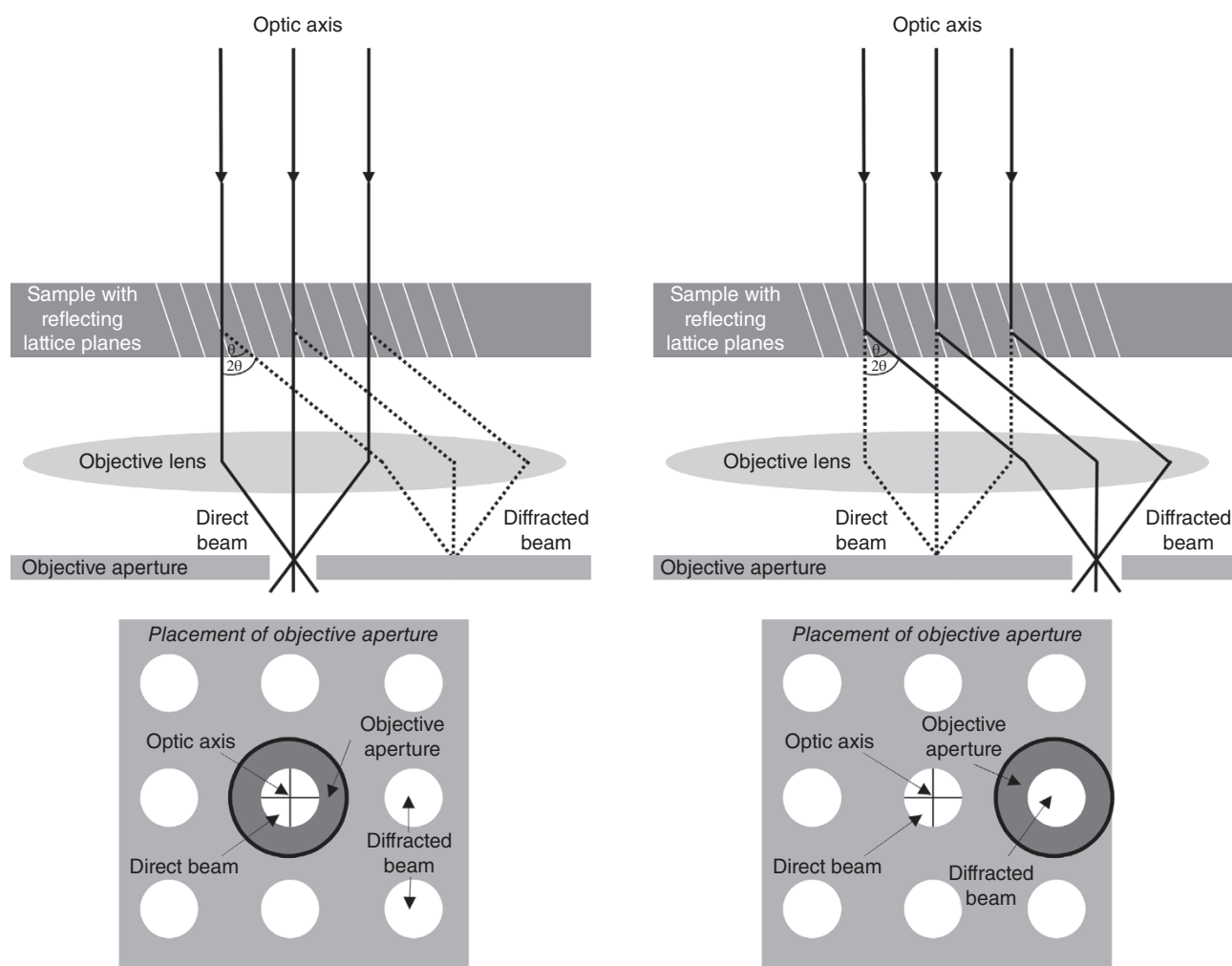


Figure 3 Electron beam paths in the parallel sample illumination mode in TEM. Left: direct beam used for imaging (bright-field imaging technique). Right: diffracted beam used for imaging (dark-field imaging technique). In both cases one selects the appropriate beam by moving the objective aperture in the back focal plane (diffraction plane).

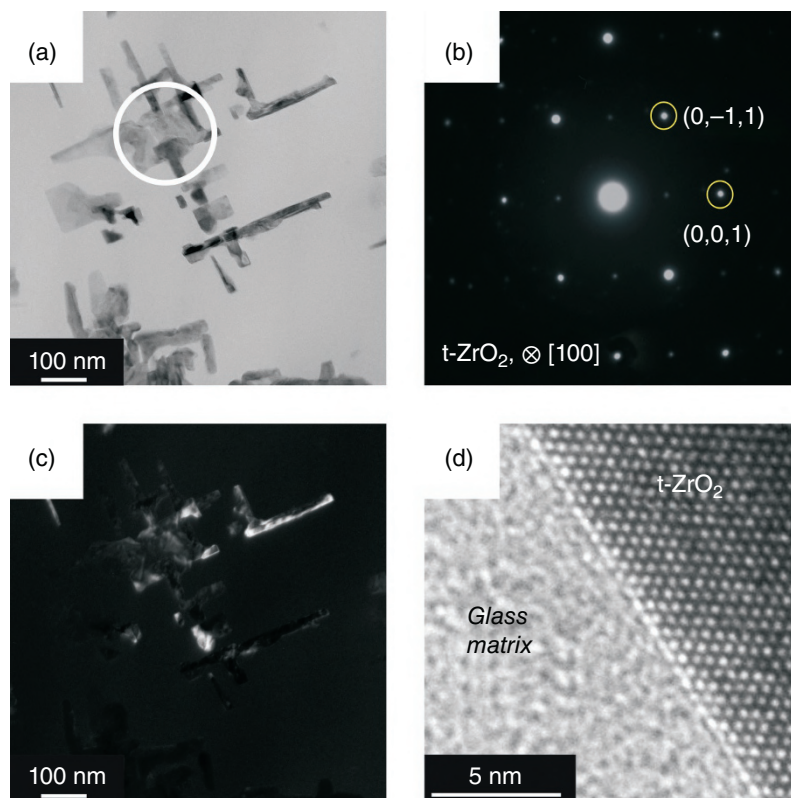
surroundings for two reasons: First, crystal lattices induce strong diffraction up to high angles, particularly when they are well aligned along a low-index crystallographic axis. Second, when these precipitates preferentially incorporate heavy elements, their cross sections for inelastic scattering are also larger than those of their glass surroundings. The effect is seen in Figure 4a for the bright-field TEM micrograph of a MAS glass ceramics similar to that discussed above for SEM (both from the same green glass, with just a different annealing such that only zirconia precipitated in that case).

As already mentioned, one can readily tune electron lenses to the desired focal length to image also the back focal (diffraction) plane. A well-oriented zirconia is revealed in this way in the MAS glass-ceramic sample (Figure 4a). Information on circular areas of less than

200 nm in diameter can even be obtained with the so-called selected area electron diffraction (SAED) aperture as illustrated in Figure 4b for the MAS sample. Indexing of the pattern further shows that the ZrO_2 crystal is aligned along the [100] direction, which unambiguously indicates its tetragonal symmetry.

Dark-field and bright-field imaging are again closely related (Figures 3 and 4c) because a small contrast-enhancing aperture can also be positioned in the diffraction plane of the objective lens in such a way that the direct (undiffracted) beam is *not* allowed to pass through it. Originating either from crystal diffraction spots or from amorphous diffraction rings, some of the diffracted intensity is allowed instead to travel further down the microscope column and form an image. Because the relatively small apertures ($>5 \mu\text{m}$) are circular holes and not

Figure 4 Transmission electron micrographs of the MAS glass ceramics. (a) Bright-field image where crystalline ZrO_2 features appear dark in a glass matrix of bright contrast. (b) Electron diffraction pattern taken from a sample area circled in (a). (c) Dark-field TEM micrograph of the same sample area. Crystal appearing bright because the objective aperture is moved away from the direct beam to allow only diffracted beams to pass by. (d) Aberration-corrected high-resolution TEM micrograph of a part of the sample where a ZrO_2 crystal has a boundary with the surrounding glassy matrix.



annular rings, dark-field imaging always catches only a fraction of the diffracted intensity, resulting in much longer exposure times and associated risk of running into drift issues. Dark-field imaging is nevertheless often useful since its sensitivity to small differences in diffracting/scattering power is clearly superior to that of bright-field imaging. In addition, it often makes a “quick survey” possible for crystalline areas in the sample. As an example, the zirconia crystals embedded in the glassy MAS matrix appear as the bright area in the dark-field image of Figure 4c, where only significantly diffracted or scattered electrons contribute to the contrast with the dark surrounding glassy matrix.

With high-resolution TEM (HR-TEM), one can image directly rows of atoms in the crystalline parts of the specimen provided that the sample is thin enough and that crystallographic directions are well aligned with respect to the optical axis, which is accomplished by phase-contrast imaging. The physics involved will not be expounded here because it is beyond the scope of this chapter, but one can think of a crystalline specimen as a weak phase object analogous to a phase grating for visible light [18]. Interatomic potentials within the crystals then affect the wave functions of the incoming electrons so that one can extract from these modifications a picture of the atomic lattice of the crystal that is visualized on a fluorescent screen or captured with a CCD or CMOS

camera. The resolution that can be obtained is well below the nanometer range, as shown in Figure 4d where a sharp boundary separates the regular crystal lattice of zirconia from the disordered atomic arrangement of the glass matrix.

3.2 Scanning Transmission Electron Microscopy

As a complement to the wealth of information on micro- and nanostructure that can be obtained from parallel-illumination-based TEM observations, one can also perform chemical analysis with modern machines, for example, by means of EDXS. In order to do so, sample areas as small as possible should be assessed directly with a finely focused probe to achieve the best lateral resolution possible. That is where scanning transmission electron microscopy (STEM) comes into play. In STEM, the sample is not illuminated with a broad parallel electron beam. Instead, the condenser lens system is used to form a fine electron beam that can be moved laterally over the sample surface with the help of deflection coils, in close analogy to what is done in an SEM. The difference is that SE emitted from the sample upon electron impingement are not detected. The primary electron beam passing through the very thin specimen of course remains used for imaging, but it loses energy through interactions with the sample atoms by either elastic

(diffraction) or inelastic scattering. Of special interest for imaging are the inelastically scattered electrons, since the resulting contrast is highly sensitive to the mass of the atoms in the specimen. The scattering cross section of that electron–sample interaction approximately varies with the atomic number Z of the screened sample atoms according to Z^a , where a is in the 1.2–1.8 range [22]. Thus, the heavier or denser the analyzed sample position, the larger the scattering angle of the primary electrons.

Usually the setup for catching the scattered primary electrons consists of a ring-shaped detector below the sample (Figure 5). In this (high-angle) annular dark-field [(HA)

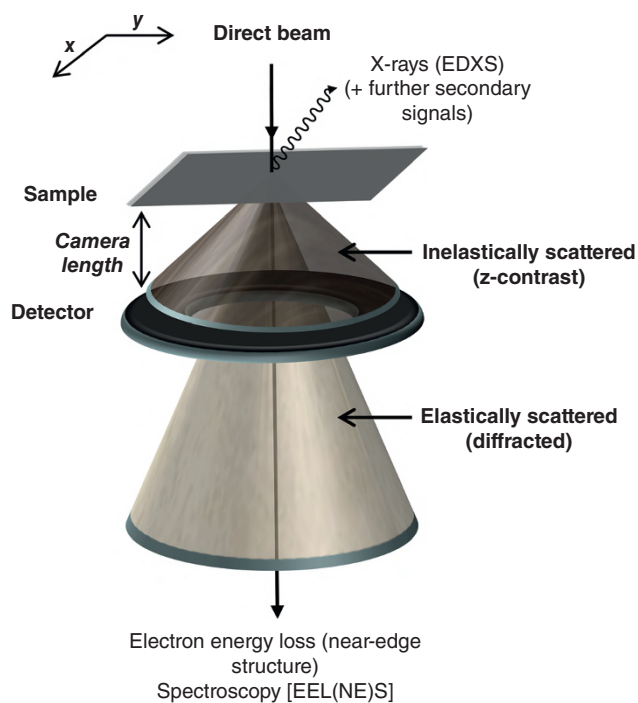


Figure 5 Working principle of the scanning transmission electron microscope.

ADF] imaging mode, the larger the scattering angle of the primary electrons, the more signal will be recorded on the detector. Thus, heavier elements in the sample generally appear as brighter features in the image. The camera length is the distance between the sample and the detector. Because one can change it easily by adjusting the electromagnetic lenses of the TEM, it is possible either to induce only Z-contrast in the image (short camera length) or to use a fraction of the elastically scattered (diffracted) electrons to gain signal on the detector (long camera length), thus incorporating also information concerning the crystallinity of the sample in the micrograph.

The MAS glass-ceramic sample may also serve to compare the images formed with TEM and STEM. In a TEM image in bright-field mode (Figure 6a), the zirconia crystals appear dark in a bright glass matrix. This contrast is caused by both mass thickness effects (i.e. stronger inelastic scattering of primary electrons and absorption of primary electrons by zirconia) and diffraction effects (elastic scattering of primary electrons by the zirconia lattice planes). On the contrary, the STEM-HAADF micrograph in Figure 6b shows bright zirconia crystals in a dark matrix because the signal collected by the annular HAADF detector from the electron beam scattered at large angles is much more intense for the heavy Zr atoms than for the relatively light Mg, Al, Si, and O atoms of the glass.

A big advantage of STEM analysis is of course that one can use the primary electron beam for other purposes than just imaging of the sample. With nanobeam diffraction, one can address areas as small as a few nanometers to generate diffractions patterns from which crystallographic structures can be analyzed in great detail, with a probe diameter lower than 5 nm, that can be moved over the sample to study specific areas with nm resolution. Just as in SEM, it is also possible to detect and analyze secondary signals emerging from the electron beam–specimen interaction, such as X-ray quanta or visible light (CL). Especially EDXS in STEM is an extremely helpful tool for a quick determination of the distribution of

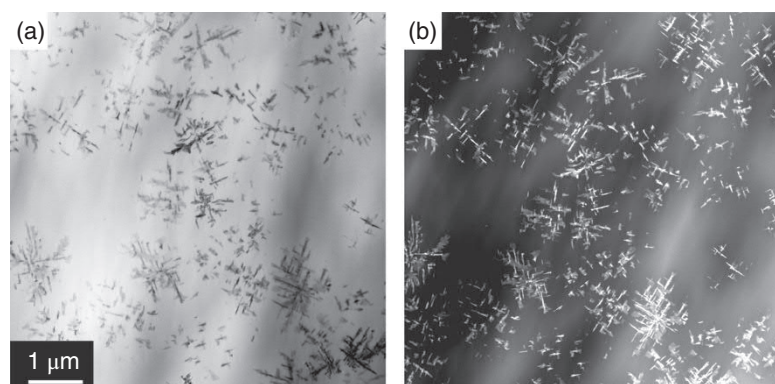


Figure 6 Comparisons of TEM and STEM images of ZrO_2 crystals in the glassy MAS matrix. (a) TEM bright-field and (b) STEM-HAADF micrographs.

chemical elements in a sample at a scale that can be truly nanometric because the sample is so thin that the excitation volume is not subjected to lateral resolution broadening: for a TEM sample thinner than 50–70 nm, the excitation volume is now just the very neck of the interaction volume shown in Figure 1. In modern (S)TEM machines, EDX detectors may cover a large solid angle (>1 steradian) above the sample, thus ensuring fast elemental analysis [23].

With these improvements, most of the problems faced with SEM for the chemical analyses of the MAS glass ceramics are readily overcome. First, there is no need to worry about excitation volume and lateral resolution of the EDX analysis since the sample is *very* thin. Second, the generally higher resolution of TEM systems enables finer details to be seen and analyzed. Third, the increased energy of the primary electron beam (here, a 300 kV acceleration voltage) allows high-energy spectral regions far beyond 10 keV to be accessed so that the $Y\text{-}K_{\alpha}$ (at ≈ 14.9 keV) and $Zr\text{-}K_{\alpha}$ (at ≈ 15.7 keV) lines can now be unambiguously separated.

One might wonder why 300 kV acceleration voltage in TEM does not cause the same charging problems as 30 kV in SEM. The reason is that in a thinner sample the interaction cross sections of a very-high-energy electron beam with matter are getting small enough that a majority of electrons can pass through without any interaction. However, this does not mean that radiation damage is not

at all an issue in TEM. Although the process has a low probability, an electron may directly hit an atom or ion and displace it in what is called a knock-on damage. Besides, one finds that glasses and glass ceramics are prone to damages caused by the electron beam, such as motion or even evaporation of Na, Li, or other volatile elements [24], amorphization, or, conversely, crystallization, to name just a few. The experimental conditions to be used (acceleration voltage, maximum beam dose, etc.) *always* depend on the particular sample investigated and often demand a great deal of expertise and experience. Whereas MAS glasses and glass ceramics are quite robust, lithium aluminosilicate (LAS) materials, in contrast, survive a TEM experiment only if irradiated with electrons of reduced energies (typically ≈ 80 kV) and then might still deteriorate readily if exposed even to moderate electron beam doses [25]. To find suitable conditions, it is thus important that large sample areas be available for testing and that settings can be adjusted and saved in the microscope computer.

An example for the use of STEM-EDXS with high lateral resolution is shown for the MAS glass ceramics in Figure 7. The distributions of selected elements are indicated in false color as evaluated from the intensity of the relevant X-ray K -lines in the pixelwise EDX spectra recorded when the beam was rastered over the sample. Even at comparably low magnification (upper panel of Figure 7), these elemental maps clearly show that spinel

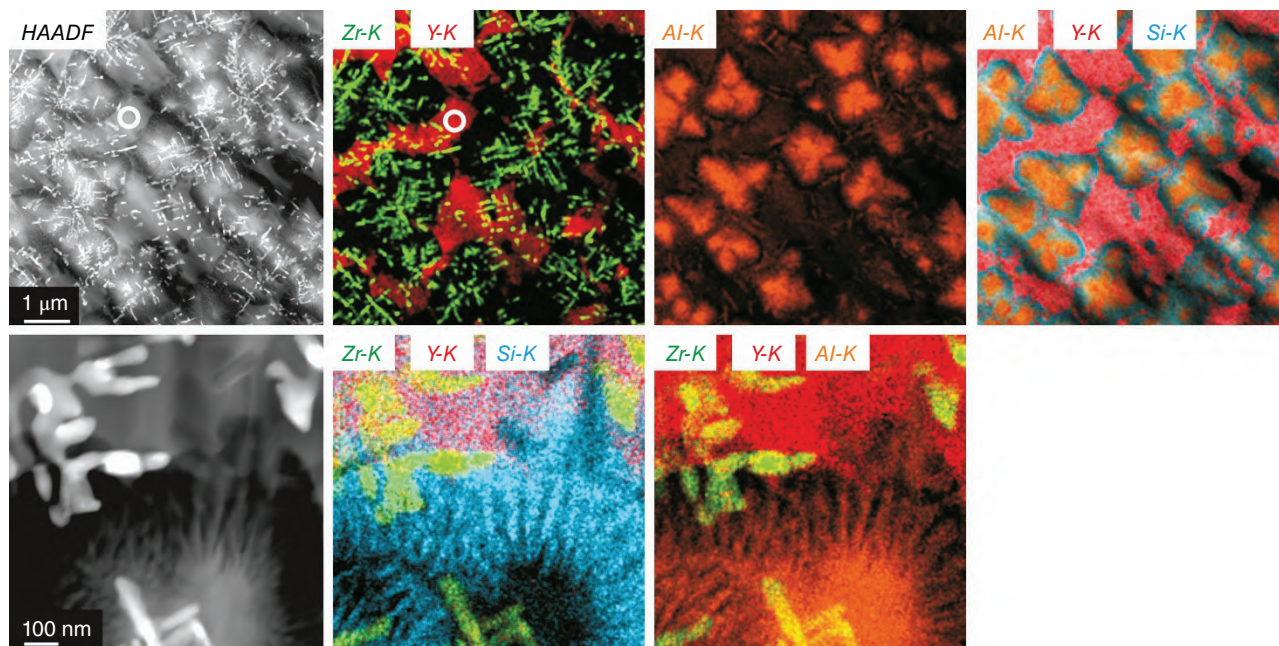


Figure 7 Micrographs of element distribution as determined for the areas shown on the left panels by STEM with a 300 kV acceleration voltage at low (upper panel) and high magnification (lower panel) from the indicated emission lines. The Zr, Al, and Y distributions map the zirconia, spinel, and glass phases, respectively. A dendritic spinel is shown in the lower panels, embedded into a silicon-rich matrix that isolates it from the actual yttrium-rich glass matrix.

Table 1 Composition of the MAS glass (at %),^a where “pristine” denotes the homogeneous, non-annealed sample and “annealed” denotes the residual glass areas in the glass ceramics after annealing.

	Mg	Al	Si	Zr	Y
Nominal	16.5	33.9	41.4	4.2	4.0
EDXS pristine	16.8	33.7	41.1	4.5	3.9
EDXS annealed	11.8	17.2	43.1	2.7	25.2

^a Oxygen not considered because of self-absorption of the low-energy O-K X-rays.

(MgAl₂O₄) is growing on dendritic zirconia as secondary phase (Al can be seen as a “marker” for MgAl₂O₄ here). Furthermore, it is obvious that Y is pushed away from the growing spinels into the residual glassy areas. But other features are also apparent, such as the existence of a silicon-enriched shell between the spinels and the residual glass. At higher magnification (lower panel), additional stunning details are seen, e.g. the dendritic structures formed by the growing spinels when they expand into the surrounding matrix.

In view of the small excitation volume in TEM experiments, it is rather straightforward to compute the relative intensity ratios of the element-specific peaks in an EDX spectra and thus to get a quantitative element distribution of tiny areas within a sample once the system is properly calibrated. In this way, crystallization-induced changes in the composition of the residual glass can, for instance, be investigated, even if the lateral dimensions of the residual glassy areas are a few nm³ only. As shown by Table 1, the STEM-EDX calculated compositions of the pristine green MAS glass are in excellent agreement with the nominal data, whereas important changes are observed after heat treatment for Zr and especially for Y.

3.3 Electron Energy Loss Spectroscopy

In analytical (S)TEM, an additional useful source of information concerns the nature, valence, and coordination of atoms, which affect specifically the energy loss undergone by the primary beam through inelastic scattering by electron clouds within the sample. As in X-ray absorption spectroscopy (XAS) or, more precisely, X-ray near-edge structure spectroscopy (XANES) (see Chapter 2.2), the interaction of a given atom with its local environment, i.e. the influence of the nearest neighbors on its electronic structure, is thus probed with an appropriate spectrometer mounted below the sample, which filters electrons according to their energy loss. This energy loss near-edge structure spectroscopy (ELNES) has certain advantages, such as a superior spatial resolution in comparison with

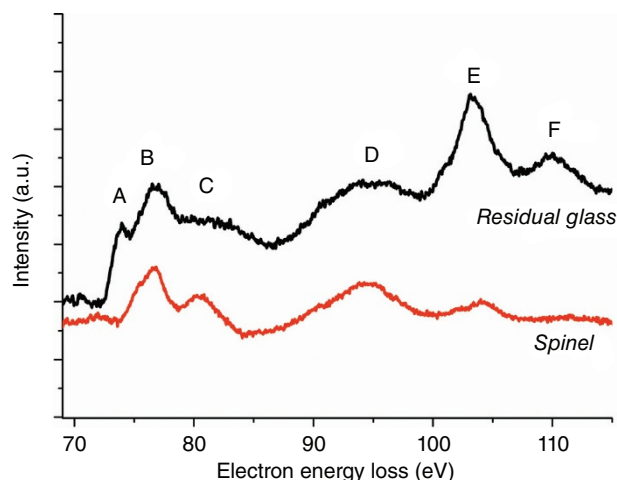


Figure 8 Al-*L*_{2,3} edge EELS spectra of MAS sample areas that represent either the residual glassy part or the spinel therein.

XANES. In addition, it is applicable to light elements such as Li, Be, or B, whereas appropriate cross sections for X-ray generation typically restricts EDXS to elements heavier than B. On the other hand, quantification of electron energy loss (EEL) spectra is not as straightforward as in EDXS, and one is restricted to energy losses lower than ≈2 keV with EELS. Thus, it complements nicely with EDXS, whose typical spectral domain for useful application starts at approximately 2 keV.

As an example, the excitation of aluminum electrons from the 2p level to empty states above the band-gap energy gives rise to Al-*L*_{2,3} edge EEL spectra where the presence, relative intensity, and energy position of specific features (A–F) bring information on Al coordination (Figure 8). For spinel, the spectrum is, for instance, typical of Al in octahedral coordination [26], which is not observed in the residual glass matrix whose detailed interpretation is actually more complicated because the features in the 100–110 eV energy range are convoluted with the Si-*L* edge signal. Although they are beyond the scope of this chapter, elaborate computation techniques nonetheless exist with which information on coordination can be derived with an increasingly high precision from the intensity and positions of the peaks in EEL spectra [5, 27]. Not all ionization edges are well suited for in-depth analyses, however, the so-called white lines of transition metals being generally favorable cases.

4 Scanning Probe Microscopy

Owing to the inherently nonperiodic arrangement of atoms in glass, use of scanning probes is of special interest for studying the topography of a sample surface and inspecting, for instance, its roughness after polishing.

Besides, information on the structure of a crystal present at the surface can be obtained, especially if some relaxation or reconstruction phenomena have caused a local change of its periodic arrangement.

Among the probe microscopy techniques that have been designed, atomic force microscopy (AFM) is probably the most widespread. Rather than describing its *noncontact* or *tapping* modes, we will restrict ourselves to the basic principle of its *contact* mode, which is sketched in Figure 9. When a cantilever is moved against the sample surface in an x - y raster scan, it is deflected differently depending on the local roughness or composition of the sample surface. Because the deflection can be monitored precisely via the reflection of a laser beam on the cantilever head, it can be kept constant with an appropriate electronic feedback loop (constant-force AFM). If this force is modulated in the z -direction with a certain oscillation frequency, the sample surface resists the oscillation, so the cantilever bends according to the stiffness of the probed sample area. With this force-modulation approach, the information obtained thus goes farther than surface topography since a certain measure of the surface elasticity is also obtained.

Again the MAS sample illustrates the results that can be obtained with AFM in terms of surface topography and hardness (Figure 10). For a polished surface, identification of the dark (glass) and bright (spinel or zirconia) areas apparent in the micrograph has to rely on SEM

or (S)TEM experiments, but the force-modulation micrograph yields information not available by other means on the much greater hardness of the crystalline phases compared with that of the glass matrix.

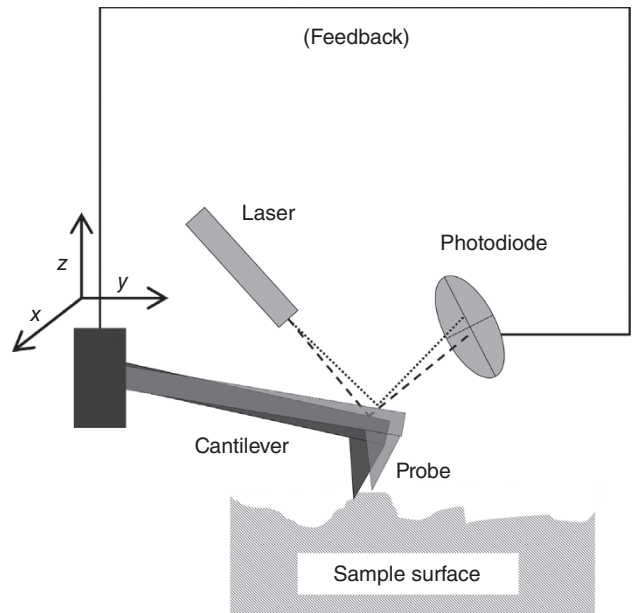
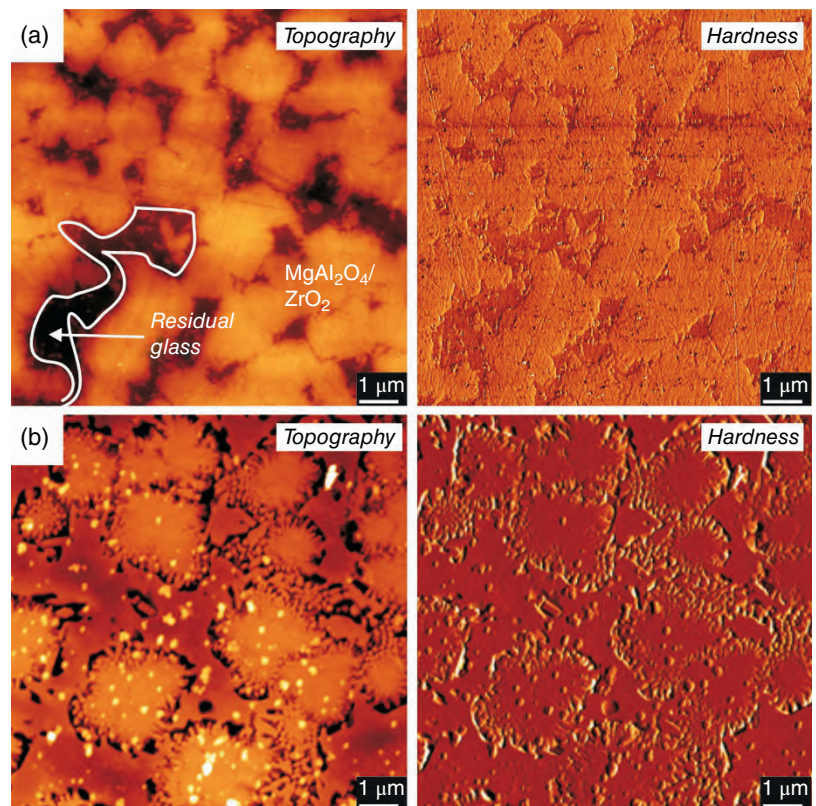


Figure 9 Working principle of the atomic force microscope in the contact mode.

Figure 10 Topography (left) and hardness (right) contrasts between spinel and the glass matrix of the MAS sample in AFM micrographs.

(a) Unetched, polished sample and (b) superficially etched sample. Hardness contrast derived from a mapping of the cantilever amplitude damping.



Because different phases are not attacked by acid solutions at the same rate, etching of glass-ceramic surfaces by HF or HF–HNO₃ solutions can enhance the microstructure contrast in AFM observations. In the MAS sample, the SiO₂-rich glass is, for instance, more prone to dissolution upon HF etching than spinel and zirconia, so the dendritic- or “finger-like” shape of the spinel growth front is more clearly seen (Figure 10b). In contrast, the large residual glassy areas that are much less etched have a different composition. Indeed, from the EDXS results described in Section 3.2, it is known that these residual glassy areas are strongly enriched in Y.

5 X-Ray Microscopy

As applied to glasses and glass ceramics, the aforementioned techniques give detailed insights into microstructures and even nanostructures. However, some difficulties remain to be faced. Like electron microscopy or scanning probe microscopy, imaging techniques usually require some sort of (often demanding) sample preparation. If preparation artifacts are avoided, one ends up with a wealth of information about morphology, chemistry, and crystallography for a sample volume of only a few 100 nm³. As stated in the Introduction, it is, therefore, highly desirable either to complement such detailed investigation down to the sub-nanometer scale with more integrating techniques or to find ways to assess larger volumes, even at the risk of losing spatial resolution.

In this respect, X-ray microscopy (XRM) has emerged as a new kind of imaging technique that is both nondestructive and capable of offering a three-dimensional (3-D) description of the sample bulk. With a maximum 3-D spatial resolution of 50 nm, it cannot compete with TEM. But sample preparation (for example, with laser micromachining) is rather straightforward, so XRM gives quick answers in the form of a 3-D density mapping of a reasonably large piece of specimen that may represent the sample bulk.

The technique is based on shadow casting of X-rays stemming from a point source and going through the sample volume to end up onto a CCD camera. It is similar to X-ray computed tomography, from which it differs by the fact that the X-rays are focused within the sample, rather than the sample being illuminated as a whole, and that the signal is further magnified optically on the screen. Because this magnification is made from the central part of the sample, image aberrations are minimized, and enhanced X-ray optics (derived from synchrotron beamlines) help to achieve an unprecedented resolution. But as with X-ray computed tomography, the acquisition of series of images for a rotating sample, followed by

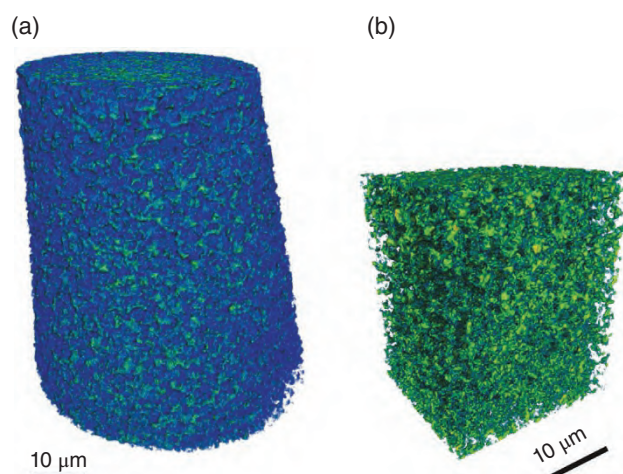


Figure 11 Three-dimensional (3-D) representation of X-ray microscopy data from a truncated cone that was laser micromachined from the MAS glass ceramic. (a) Entire dataset with denser volumes in brighter contrast (green in the false color version) and lighter volumes in darker contrast (blue in the false color version). (b) 3-D visualization of just the high-density regions of the sample, taken from a clipped internal volume of (a) to make segmentation easier. Volume fractions: dense inclusions: 23%, lower-density material: 77% (see electronic version for color figures).

image processing of the resulting datasets, can yield 3-D pictures.

For the MAS sample repeatedly considered here, such a 3-D picture clearly shows how the high- and low-density components are interconnected (Figure 11), the former and latter likely being the Y-bearing glass and the spinel, respectively. Owing to a lack of elemental and spatial resolution, however, yttria in the residual glass and the zirconia needles cannot be discerned.

6 Perspectives

This review of microstructural techniques is not comprehensive. In addition to the variety of spectroscopy techniques such as IR, Raman, XPS, or micro-X-ray fluorescence (Chapters 2.2 and 5.1), which also possess certain spatial-resolution capabilities, electron backscatter diffraction, transmission Kikuchi diffraction for texture analyses, or time-of-flight secondary ion mass spectrometry can also be used to investigate the property–structure relationships in glass-based materials down to a sub-nanometer scale. Because an important feature shared by all of these techniques is their ever-improving resolution and analytical precision, one can expect a better understanding of the way in which valuable mechanical, thermal, optical, or electronic properties are achieved in inhomogeneous materials. Conversely, these observations should help to

design and tailor new materials for specific applications. Of particular interest is a better understanding of crystallization processes, whereby the nucleating phases not only differ generally in chemical composition from the starting glass but can be nonstoichiometric and highly disordered. In this respect, more detailed observations thus should serve as a basis for theoretical investigations in the fascinating field of the coordination and valence changes that are taking place during microstructure evolution. And one can even expect that further instrumental advances will make it possible to check material properties online during glass and glass-ceramic fabrication and figure out at once causes for production failure, such as surface devitrification.

Acknowledgments

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2.4

Short-range Structure and Order in Oxide Glasses

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1 Introduction

Information about short-range structure is crucial for understanding, predicting, and optimizing the physical and chemical properties of oxide glasses. Glass structures also provide first approximations for the high-temperature molten precursors of these materials, whether in a glass melting tank or a natural magma system, and thus give fundamental information for understanding and predicting liquid properties [1, 2]. Glasses are often simply categorized as “disordered” solids, lacking the long-range order and the accompanying Bragg diffraction peaks of their crystalline counterparts. The nature and extent of this disorder, however, and how these vary with composition, temperature, and pressure, are of key importance. Much is now qualitatively known about such questions, but quantitative understanding is in many cases just beginning.

Because the same short-range bonding interactions are present in crystals, glasses, and liquids, a sensible starting point for discussions of oxide glass structure is often that of known crystalline compounds. However, this approach has limitations and can be downright misleading. An example is shown in Figure 1, which compares the oxygen ion environments of crystalline and glassy CaTiSiO_5 (titanite), a compound with a particularly high entropy of fusion [3]. Some of the same short-range structures are present in both, but the glass (and thus liquid) has not only quantitatively greater ranges in local structural variables but major qualitative differences in the type and variety of atomic-scale environments. Furthermore,

these types of data typically do not reveal the degree of mixing among the various structural groups, which thus leaves the interesting problem of possible medium-range heterogeneities unanswered.

In this chapter, we begin with a brief summary of the short-range structures of well-known single-component network oxide glasses, and compare and contrast the different mechanisms by which addition of network modifiers cause rearrangement of these structures. We then continue with the type and degrees of order/disorder that result from mixing of multiple modifier and/or network cations in multicomponent glasses and liquids. Silicates, aluminosilicates, borates, germanates, and phosphates are emphasized as these are most common in nature and in technology. However, it is important to note that other glasses, based on oxides that also have small, highly charged cations and that thus can behave as “network formers” in some ranges of compositions, can provide intriguing clues as to important principles of glass structure/property relationships. These include (at least) TeO_2 , As_2O_5 , V_2O_5 , Sb_2O_5 , CrO_3 , and MoO_3 .

2 One-component Oxide Glass Formers

Pure SiO_2 , GeO_2 , and B_2O_3 readily form glasses on cooling from the melt, and epitomize the “network-forming” oxides. The Si^{4+} , Ge^{4+} , and B^{3+} cations all have high valences, relatively high electronegativities, and are small enough to be stable in four- and/or three-coordination with oxygen. The strongly bonded and interconnected structure that results contributes to high liquid viscosities, slow diffusion, and crystal growth rates, and thus good glass-forming ability.

Of the three pure-oxide glass formers, silica is by far the best studied because of its many important technological

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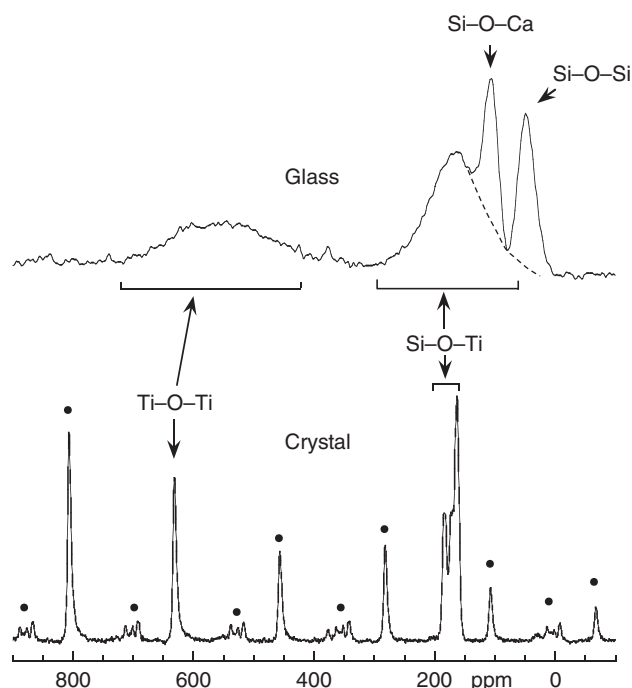


Figure 1 Oxygen linkages in crystalline and glassy CaTiSiO_5 as seen by ^{17}O MAS (magic-angle-spinning) NMR. Ti–O–Ti and Si–O–Ti oxygens are abundant in both, but peaks are much narrower in the crystal because of the long-range order, whereas the glass contains much greater local-scale disorder. The glass also contains abundant structural groups absent from this crystal, such as Si–O–Si and Si–O–Ca oxygens, requiring a more complex structure. Spinning sidebands are marked by black dots. *Source:* Modified from [3].

applications, although many of its properties are anomalous with respect to multicomponent silicate glasses. The structures of the multiple (low pressure) crystalline forms of silica are all comprised of three-dimensional networks of corner-shared tetrahedra linked by Si–O–Si “bridging oxygens” (BO). Early X-ray scattering results confirmed this coordination in the glass and yielded mean Si–O bond distances similar to those in the crystals (Figure 2) [4], as have many subsequent diffraction and spectroscopic studies. The short-range disorder is most obvious in distributions of Si–O–Si bond angles, which have been determined from methods such as X-ray and neutron scattering, vibrational spectroscopy, and ^{29}Si and ^{17}O NMR. This disorder is in turn related to distributions in the sizes and connections among the rings that can be mapped in structural models. The lack of other major sources of disorder is probably why the entropy difference between the liquid and crystal is the lowest known for any oxide [5].

Ambient-pressure crystalline borates are known to contain both BO_4 tetrahedra and BO_3 triangles, whereas pure B_2O_3 consists only of the latter. Early X-ray scattering

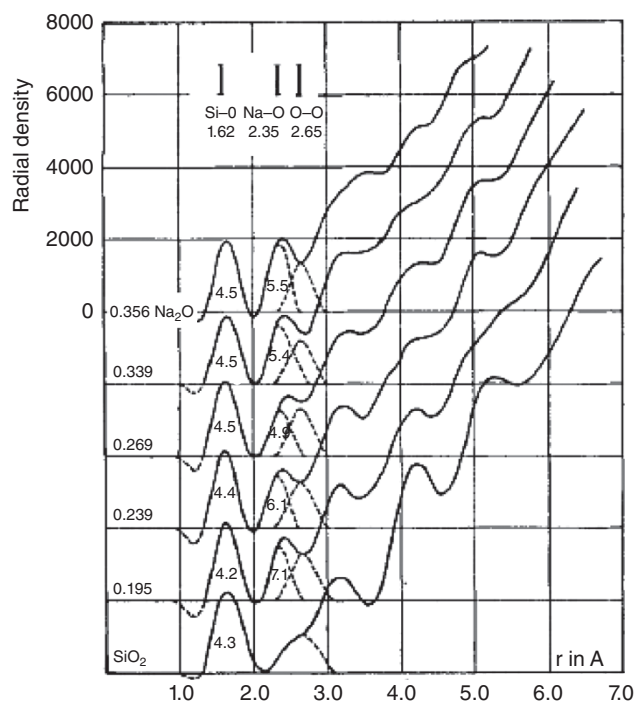


Figure 2 Radial distribution curves derived in an early X-ray scattering study of Na_2O – SiO_2 glasses, with mole fractions of Na_2O labeled. Estimated coordination numbers for Si–O (recognized by the authors to be equivalent to 4.0) and Na–O are shown under the corresponding peaks, and mean interatomic distances are shown above the curves. *Source:* Reprinted with permission from [4].

studies again were fundamental to understanding the glass, which also contains only the three-coordinated species. Subsequent evidence, from diffraction and spectroscopy, confirms this conclusion. A long controversy over how the BO_3 triangles are interconnected has largely been resolved in favor of abundant three-membered “boroxol” rings (Figure 3), thanks to methods such as combinations of neutron and X-ray diffraction with structural modeling and sophisticated two-dimensional (2-D) and multinuclear NMR. These have been applied in more complex compositions as well (Sections 3–5). Pure GeO_2 can take on both tetrahedral and octahedral structures even in ambient-pressure crystals, and compounds such as alkali germanates often contain mixtures of GeO_4 , GeO_6 , and even GeO_5 groups. Diffraction and spectroscopic studies agree that pure GeO_2 glass at ambient pressure is comprised mostly or entirely of tetrahedral groups and is thus a good analog for SiO_2 . In-situ X-ray absorption spectroscopy (XAS) and diffraction experiments on both SiO_2 and GeO_2 glasses at tens of GPa pressures indicate substantial bond lengthening for both Ge–O and Si–O and increases in Ge and Si coordination numbers, these effects taking place at much higher pressures for Si than for Ge.

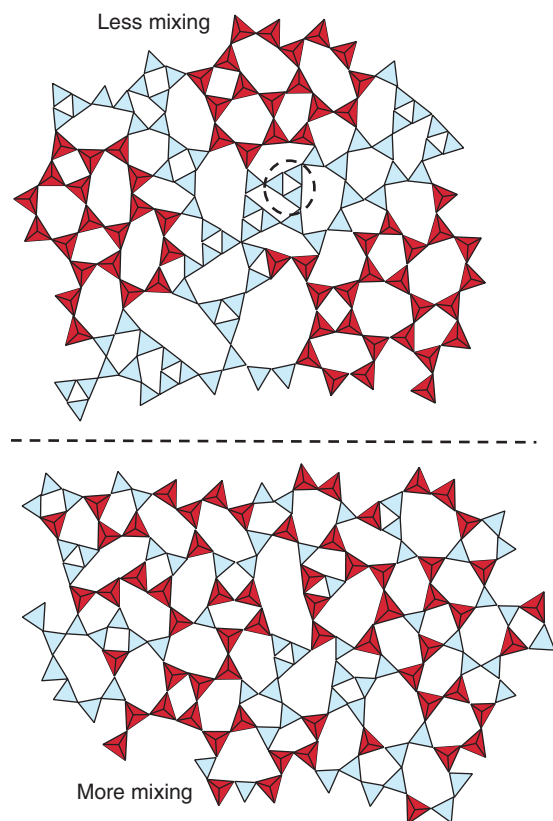
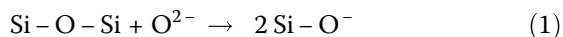


Figure 3 Two-dimensional sketch of a mixed network oxide glass such as $\text{B}_2\text{O}_3\text{--SiO}_2$. “Boroxol” groups (a typical one is circled) are particularly abundant in pure B_2O_3 glass. Another aspect of the disorder is the degree of mixing of network cations, which can be determined by methods that “count” the number of different oxygen bridges, e.g. between BO_3 groups (light color) and SiO_4 units (darker color).

3 Modifying the Network: Silicates and Phosphates

When an oxide of a larger, lower charged cation (e.g. Na_2O or CaO) is added to liquid silica, the oxide ion (O^{2-}) can interact with network oxygen bridges between SiO_4 tetrahedra to form “non-bridging” oxygens (NBO), as symbolized by a reaction illustrated by Figure 4:



Results from even the earliest X-ray scattering studies of alkali silicate glasses (Figure 2) supported this basic concept [4]. Likewise, many vibrational spectroscopy studies have demonstrated increasing proportions of NBOs within silicate tetrahedra with increasing modifier contents. “Network-modifier” cations such as Na^+ and Ca^{2+} balance the negative charge on each of the NBOs: bond-valence considerations generally require several such cations for each NBO as seen in the corresponding

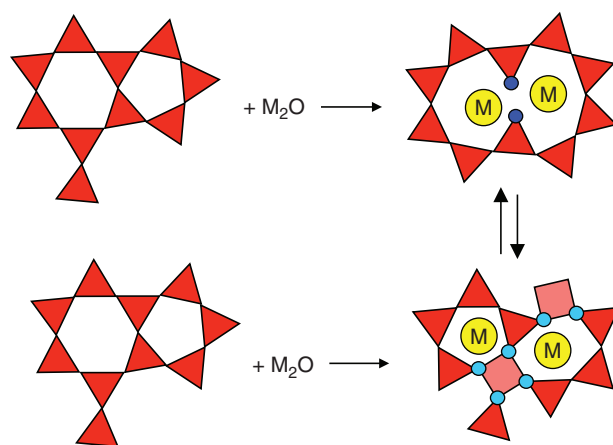


Figure 4 Two-dimensional representation of the modification of a glass network induced by addition of an alkali oxide M_2O . The SiO_4 , BO_3 , GeO_4 (etc.) polyhedra are symbolized by the triangles. (top) Conversion of one bridging oxygen to two non-bridging oxygens (small, dark circles), which are charge balanced by the alkali cation (large circles). (bottom) Increase in the coordination numbers of two network cations (squares) and the formation of bridging oxygens with partial negative charges (small, light circles). Conversion between these two types of modified network, with either pressure or composition, is indicated by the vertical arrows.

crystals. At low modifier concentrations, there are not enough NBOs to fill the coordination sphere of each modifier, with typically five to eight oxygens needed. This means that without cation clustering to allow nonrandom sharing of NBOs, some BOs must also serve this coordinating role. With higher field strengths of the modifier cations (defined as the formal charge divided by the square of the mean cation–oxygen distance), this arrangement is increasingly unstable and can lead to liquid–liquid phase separation over wider ranges of composition. With very high field-strength modifiers (e.g. La^{3+} , Zr^{4+}), or for cations with relatively high electronegativities (e.g. Sn^{2+} , Pb^{2+}), the structural and chemical distinctions between BO and NBO may begin to blur, in that some “modifier” cations may take on low coordination numbers and $\text{Si} - \text{O} - \text{M}$ linkages may become relatively strong. Such cations are often described as having “intermediate” character.

Reaction (1) can also be considered as a description of chemical equilibrium among oxygen ion species, and has long played a prominent role in models of the thermodynamics of low-silica metallurgical slags. Conventional views have suggested that “unreacted” or “free” oxide ions are probably only abundant in low-silica glasses and/or in systems with highly electronegative modifiers such as Sn^{2+} and Pb^{2+} . Oxygen ion speciation in some silicate glass compositions can be measured with methods such as XPS and ^{17}O NMR, or estimated indirectly through techniques that provide information on silicate anionic

speciation such as Raman spectroscopy and ^{29}Si NMR (see Section 7.2). Some such studies have suggested the presence of a few percent of “free” oxide ions in compositions well outside the range where they are required by stoichiometry alone, e.g. at silica contents >33.3 mol% in the MgO-SiO_2 binary. As containerless melting and quenching methods have made the formation of very low silica glasses possible (even into the “sub-orthosilicate” range, e.g. lower silica than in Mg_2SiO_4), it has become possible to quantify more clearly this most basic aspect of silicate structure [6].

In “modified,” ambient-pressure silicate glasses, only tiny fractions of SiO_5 groups have been detected in a few alkali silicates. However, high pressures, or high P_2O_5 contents, can lead to the formation of substantial fractions of both SiO_5 and SiO_6 , which will contribute to the overall network disorder as well as to density increase. For example, both an unusual high-pressure crystalline phase of CaSi_2O_5 and its glassy equivalent clearly have all three Si coordinations (Figure 5). A number of in-situ, high-pressure studies, particularly by Raman spectroscopy, have suggested that considerable structural relaxation, and reversion to lower network cation coordination, can take place on decompression of a glass, even at ambient temperature. A few of these have probably also taken samples above T_g at high pressure. The small cationic radius and high charge of P^{5+} makes P_2O_5 another well-known network-forming oxide. Over wide

ranges of composition, two-component and more complex phosphate liquids are stable and can be quenched to glasses. These have been extensively studied, particularly by vibrational spectroscopy and ^{31}P MAS NMR. All phosphorus is present in PO_4 tetrahedra. As in silicate glasses, these are linked together to form chains of varying length as well as more complex structures. The roles of BO and modifier oxides in phosphate glasses are analogous to those in silicates, as are the considerations of anionic speciation discussed in Section 7.2.

4 Modifying the Network: Borates and Germanates

Contrary to what is found in ambient-pressure silicates and phosphates, a different type of network modification takes place when oxides of low-valence cations are initially added to B_2O_3 or to GeO_2 , facilitated by the energetically “easy” transitions of network cations between two (BO_3, BO_4) or even three ($\text{GeO}_4, \text{GeO}_5, \text{GeO}_6$) coordination states. Instead of only forming NBOs, the added oxide ion serves primarily to increase the coordination number of the network cation so that the network remains fully connected by BO, if the definition of the latter is expanded to include linkages with the higher-coordinated network cations. (It is important to note, of course, that oxygen bridges between network cations may be energetically quite distinct, and have differing implications for bulk properties, as the network cation coordination varies.) If NBOs do form, their concentrations are much lower than produced in the corresponding silicate equilibria. The “modifier” cations are coordinated primarily by BO, some of which will have partial negative formal charges, e.g. $-1/4$ on the BO linking a BO_3 with a BO_4 group. This mechanism (Figure 4) predominates up to about 20–30 mol% modifier oxide, at which point the formation of “normal” NBOs, as in silicates, begins to become important. At least part of this turnover may result from the difficulty of packing enough low-charge modifier cations around BOs with higher formal charges, i.e. $-1/2$ on the link between two BO_4 groups, and in turn this can be affected by the cation field strength and dilution of the borate network by silica. At higher modifier contents, much or even most of the network cation coordination returns to the lower state, BO_3 or GeO_4 . These compositionally induced transitions in the network cation coordination are generally mirrored in the structures of the binary crystals, and result in strongly nonlinear property–composition relationships in both the melts and glasses, e.g. density and glass transition temperature.

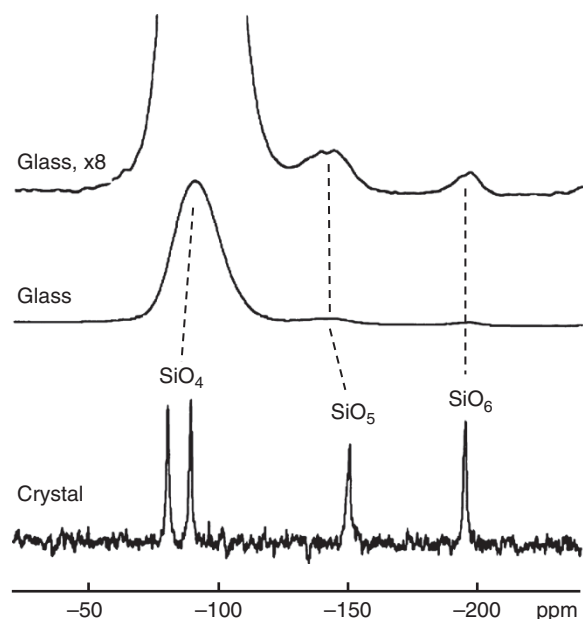


Figure 5 Silicate structural groups in a high-pressure, triclinic crystalline phase of CaSi_2O_5 and in its isochemical glass quenched from the melt at 10 GPa, showing the correspondence of signals for Si with 4, 5, and 6 oxygen neighbors in ^{29}Si MAS NMR spectra. Source: Modified from [7].

This mechanism is most precisely defined in alkali borate glasses, for which ^{11}B NMR has long been applied to measure directly BO_3 and BO_4 contents [8]. Raman spectroscopy can also detect this coordination shift, and can be more readily applied at high temperatures and pressures. The structural transition with composition can be symbolized by the reaction, which incorporates the reaction of O^{2-} with BOs to form NBOs:



This reaction can also be taken as a statement of chemical equilibrium among melt species. Shifts with temperature have been determined from both in-situ, high-temperature vibrational and NMR spectroscopy and studies of glasses prepared at different cooling rates and thus with different fictive temperatures [9]. The lower coordination state (left hand side) is generally favored at higher temperature, meaning that the enthalpy change for the reaction as written is negative. In boron-rich systems, this coordination change can be a major contributor to the overall configurational heat capacity and enthalpy of the liquid; changes in the abundances and mixing of the boron coordinations will clearly affect the configurational entropy as well. At least in borosilicate glasses, modifier cations with higher field strengths tend to favor the formation of NBOs and thus lower boron coordination numbers. Spectroscopy on quenched, decompressed glasses has shown that this mechanism leads to boron coordination increase at high pressure [10]; a few in-situ studies by X-ray and other methods have observed this process more directly.

Analogous structural transitions that take place as modifier oxides are added to GeO_2 . Alkali germanate glasses and melts have density maxima at roughly 15–20% M_2O , the compositions near which crystal structures are made up of mixtures of GeO_4 , GeO_6 , and even GeO_5 groups. Although these groups cannot be individually quantified in glasses as readily as those in boron-containing compositions, XRD and neutron diffraction demonstrate the accompanying changes in mean Ge–O distances. Also, ^{17}O NMR can distinguish BOs, NBOs, and other species in germanates and confirms the transition from a primarily “borate-like” mechanism at low modifier contents (mixed low- and high-coordination of Ge, most or all BO in the broad sense of the term) to a “silicate-like” mechanism (GeO_4 and “normal” NBO formation) at high modifier contents. Germanate crystals, glasses, and melts are often considered as at least rough analogs for silicates at elevated pressures. If the changes in network cation coordination with composition are as complex in silicate melts at high pressures, then highly nonlinear compositional effects on melt properties may be expected.

5 Network Cations in Aluminosilicates

In most readily formed multicomponent oxide glasses, Al^{3+} is a network former predominantly present as AlO_4 tetrahedra. The latter are compositionally equivalent to $\text{AlO}_{4/2}$ if oxygen sharing is taken into account. Because the alumina chemical component (Al_2O_3 or $\text{AlO}_{3/2}$) has insufficient oxygen to form this species, one NBO, if present, will be converted to a BO for each added Al cation. Simple models of aluminosilicate melt structure have long assumed that, when alumina contents become large enough to balance all of modifier oxides (e.g. moles of Al_2O_3 = moles of Na_2O or CaO), NBO contents are reduced to zero and the glass or melt structure is comprised entirely of fully connected tetrahedra, by analogy with framework aluminosilicate crystals such as feldspars (e.g. $\text{NaAlSi}_3\text{O}_8$, $\text{CaAl}_2\text{Si}_2\text{O}_8$). This is a good approximation in some systems, especially those with alkali oxide modifiers only, and is supported by long-known changes in properties with composition as well as diffraction and spectroscopic data. As alumina is added to alkali silicate melts and glasses, for example, the alkali cations are coordinated by fewer NBOs and more BOs, some of which will have partial negative formal charges, e.g. $-1/4$ for Si–O–Al and $-1/2$ for Al–O–Al. This change in role can be described as a transition from “network-modifying” to “charge-compensating” cation.

However, detailed spectroscopic studies, especially by ^{27}Al and ^{17}O NMR and Raman, show that the structure can be more complex than indicated by this model, particularly in systems with modifier cations of high field strength. In Ca and Mg aluminosilicates, for example, significant concentrations of AlO_5 (typically 4–8% of Al cations) and even small amounts of AlO_6 groups are present throughout most of the glass-forming regions [11]. Some NBOs also persist well into the peraluminous compositional range (e.g. with moles of $\text{Al}_2\text{O}_3 > \text{CaO}$). Trivalent modifier cations such as Y^{3+} and La^{3+} promote this shift in Al coordination, which increases even more obviously in peraluminous compositions and in aluminoborates and aluminophosphates. The mixing of these Al coordinations in the network must contribute to configurational entropy and related properties. As noted in Section 3, the distinction between “bridging” and “non-bridging” oxygens becomes blurred as network cations increase in coordination number and their bonds to oxygen lengthen and weaken, complicating simple structure–property hypotheses. A few in-situ X-ray diffraction and Raman studies, and more detailed research on quenched, decompressed glasses, have clearly shown increases in Al coordination with pressure, which occurs more readily than for Si. NMR studies of glasses quenched

from high-pressure melts have shown that Al coordination increase is promoted by modifier cations with higher field strength [10].

6 Short-range Order and Modifier Cations

The relatively large, low-charge cations that can serve as “network modifiers” in oxide glasses comprise much of the periodic table, so that their behavior can only be generally summarized here. Information about their local structural environments has been most commonly obtained from XAS, both XANES and EXAFS [12], from optical spectroscopy for many transition metal and rare earth cations, from Mössbauer for Fe^{2+} and Fe^{3+} , and from modeling of neutron and X-ray diffraction data. In a few cases, notably for ${}^6\text{Li}$, ${}^{23}\text{Na}$, ${}^{25}\text{Mg}$, and ${}^{207}\text{Pb}$, NMR has begun to contribute as well. In a number of oxide glass systems, the possibilities of substitution of isotopes of modifier cations with different neutron scattering cross sections (e.g. ${}^{44}\text{Ca}$ – ${}^{40}\text{Ca}$) has allowed cation-specific pair distribution functions to be derived from differential measurements, which can give unique details of ordering out to several cation shells. All of these types of data usually indicate some disorder in the first shell and, in some cases, mixes of cation coordination. Most commonly, coordination numbers are similar to those of known crystals or somewhat lower, as can be expected from the lower densities of the glass and liquid phases. Fitting of EXAFS data for some modifier cations has provided important clues about cation first neighbors and on whether these mix randomly, which can be important not only for thermodynamic models but for optical and magnetic properties. In systems with strong nuclear dipolar couplings, such as for ${}^{23}\text{Na}$ and ${}^7\text{Li}$ in alkali silicate and borate glasses, detailed studies of NMR line shapes and relaxation can give estimates of mean distances among the modifier cations [13]. With these data one can discriminate between models of random, spatially homogeneous distributions and of nonrandom arrangements with shorter average cation–cation separations. The latter feature is found in models in which modifiers are clustered in regions with relatively high NBO concentrations, for example, those in 2-D “channels” thought to be important in ion transport [1].

The coordination number of a given modifier cation often depends on glass composition. For example, the coordination number of an alkali cation should increase as the fraction of coordinating oxygens that are NBO (vs. BO) decreases with increasing silica or alumina content, and thus the negative charge per oxygen is reduced. This type of change has been measured by ${}^{23}\text{Na}$ NMR and other methods. In cases where glass color is caused by electronic transitions in cations such as transition

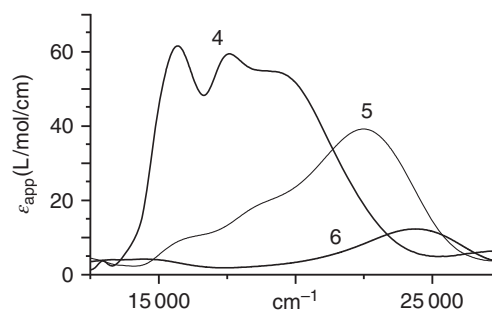


Figure 6 Optical spectra for glasses in which Ni^{2+} coordination changes from primarily 4 to 5 to 6 coordinated as alkali content is decreased. The bulk glass color changes from purple to brown to green. Source: Modified from [14].

metals and rare earths, changing site geometry or coordination number with composition can have dramatic visible and spectroscopic consequences (Figure 6). If more than one modifier cation is present in the system, that with the higher field strength can outcompete another with a lower field strength for coordination by NBOs, displacing the latter cations into sites with higher coordination number (and/or to those with more BOs) as composition changes. This type of site ordering is probably part of the explanation for the commonly seen “mixed alkali” effects, where cation diffusion and ionic conductivity can be slowed by orders of magnitude relative to those in single-modifier compositions. At higher temperatures, increased disorder with respect to modifier cations can be a major contributor to configurational entropies and is marked, for example, by the enhancement of the entropy of fusion of diopside ($\text{CaMgSi}_2\text{O}_6$) relative to those of enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) and wollastonite ($\text{Ca}_2\text{Si}_2\text{O}_6$) [2].

The charges and sizes of network-modifier cations, as in part captured by their field strength and reflected by their coordination numbers, can have huge effects on the network structure of oxide glasses and on both glass and melt properties. When the coordination of the network cation can readily change, as for boron and aluminum in some systems, higher field-strength modifiers can either decrease (B) or increase (Al) the network cation coordination, again probably through a process of formation of and/or competition for NBOs. These effects are much less well known, but could be expected in germanates and in high-pressure silicates.

7 Interactions of Network Modifiers and Network Order/Disorder

7.1 Order and Disorder of Bridging and Non-bridging Oxygens

In oxide glasses with more than one type of network-forming cation, NBOs and BOs could be equally

distributed on all such cations, or could be ordered in some way. The latter is generally the case. Raman spectra of aluminosilicates have suggested that most NBOs are on Si and that most AlO_4 groups thus have four BO, when composition permits. This result has been directly confirmed by ^{17}O NMR in Ca aluminosilicates. Comparable studies in a few borosilicates have observed B-NBO and the predominant Si-NBO.

For systems with more than one type of modifier cation, large differences in size or charge might be expected to lead to some kind of ordering. This can be sampled by methods that “see” the coordination environments of oxygen species directly. For example, both one- and two-2-D ^{17}O NMR spectra have shown that chemical shift distributions in mixed Na/K and mixed Ca/Mg silicate glasses are consistent with random distributions of the two cations around the NBOs, consistent with deductions from viscosity measurements and estimated configurational entropies. In contrast, the large field-strength difference between K^+ and Mg^{2+} leads to a concentration of the latter around the available NBO sites. This approach has shown the considerable complexity of order/disorder patterns that can occur in the distributions of modifier- and charge-compensator cations around both NBO and BO sites in a number of other mixed-cation silicates and aluminosilicates. Decreases in this type of ordering might be expected from entropic considerations at higher temperatures in the liquids.

7.2 Q^n Speciation

In silicate and phosphate glasses, the best-known aspect of network order/disorder, as affected by the modifier cations, involves the distributions of the NBOs. One can sample these distributions by counting the proportions of “ Q^n ” species, defined as tetrahedral groups with n BOs and $4-n$ NBOs. Such measurements were originally done by Raman spectroscopy [2]. At least in some simple systems such as alkali silicates and phosphates, these proportions can often be readily quantified by ^{29}Si or ^{31}P NMR; such results can be used to evaluate cross sections for vibrational spectroscopy as well. In both approaches, peak fitting and associated assumptions about line shapes are usually required and can lead to some ambiguity. An early and important question was whether the number of Q^n species present in a glass was the minimum derived from stoichiometry (in general two, but only one at special compositions), or whether entropy induced a greater variety. The clear detection of Q^2 , Q^3 , and Q^4 species in glasses such as $\text{Na}_2\text{Si}_2\text{O}_5$, which could contain only Q^3 as in the crystal, confirmed the latter view. Simple equilibria among Q^n species can be defined for $n = 1, 2, 3$:



Apparent equilibrium constants k_n for such reactions have been evaluated from Raman and NMR data on glasses, including 2-D ^{29}Si NMR on Ca and Mg silicates [15]. Higher field-strength modifiers push these reactions to the right (increasing k_n), presumably favoring the concentration of more NBOs around some Si sites and thus better local charge balance for small, highly charged modifiers. More Q^4 species are also generated, which correlates with higher thermodynamic activities of silica as deduced from phase diagrams [5]. In the range of observed speciation, greater k_n values lead to greater contributions to the configurational entropy if models of random mixing of the Q^n species are considered. But enhanced ordering of NBOs around higher field-strength cations could counter this effect to some degree and, in the extreme, could lead to cation clustering and even incipient phase separation. Shifts of such equilibria have been measured with both in-situ high-temperature Raman spectroscopy and NMR on glasses with increasing fictive temperatures, the results from the two methods often agreeing well. Estimated enthalpies of reaction are usually positive, but are less so for higher field-strength cations. If a random model is assumed (which can in some cases be tested by NMR methods yielding spatial correlations of different species), mixing of observed Q^n populations can contribute a substantial fraction of the calorimetrically determined entropy differences between glasses and crystals.

Complementary to these results for glasses in the normal, high-silica, glass-forming range are the recent findings for orthosilicate (e.g. Mg_2SiO_4) and even “sub-orthosilicate” glasses formed by quenching in laser-heated, gas-levitated, containerless melting systems. Here, significant concentrations of Q^1 species can be observed by Raman and ^{29}Si NMR, requiring as well the presence of nonstoichiometric “free oxide” ions. Direct evidence for the latter can be seen in ^{17}O NMR spectra [6].

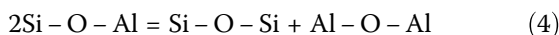
7.3 Order/Disorder in Network Linkages

The distribution of network cations (e.g. Si^{4+} , Al^{3+} , B^{3+} , P^{5+}) around BO in multicomponent oxide glasses and melts is in principle relatively simple to characterize, as each BO has only two such neighbors. This is a quite important problem, though, as it defines the extent of disorder among the various network components as well as the partitioning of partial charges on the BO, which in turn affects ordering of modifier or charge-compensator cations. Multiple-quantum ^{17}O NMR has allowed such distributions to be directly quantified in some systems, through direct counting of proportions of different linkages among network species.

In crystalline, framework aluminosilicates such as feldspars and zeolites, diffraction and NMR studies have generally shown that Al–O–Al linkages are “avoided”, if

stoichiometry allows, leading to a high degree of ordering when Al/Si = 1, as for example in anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and nepheline (NaAlSiO_4) in which all the oxygens are present as Si–O–Al linkages. This ordering presumably is related to the energetic and/or geometric unfavorability of bringing enough of the charge-compensating cations close to the relatively highly charged (formally $-1/2$) Al–O–Al linkages. There are notable exceptions for disordered crystals formed by rapid devitrification of glasses (e.g. cordierite $\text{Mg}_2\text{Al}_5\text{Si}_4\text{O}_{18}$ and β -eucryptite LiAlSiO_4), and stable tetrahedral framework compounds containing only Al–O–Al linkages are well known (e.g. CaAl_2O_4).

Triple-quantum ^{17}O NMR spectra of alkali aluminosilicate glasses can fully resolve Si–O–Si, Si–O–Al, and Al–O–Al sites. This has enabled more precise formulations of the thermodynamics of equilibria such as:



In terms of distributions of residual negative charges on oxygens, this reaction is analogous to that for the Al-free system (Eq. 3), as one species on the right has a reduced net negative charge (Si–O–Si or $Q^n + 1$) whereas the other has an enhanced charge concentration (Al–O–Al or $Q^n - 1$). In NaAlSiO_4 glass, the observation of about 10% of Al–O–Al confirmed that aluminum avoidance is not perfect, but also that this aspect of the structure is closer to ordered than to fully disordered, at least near the glass transition temperature. Further studies of other Na, Li, and Ca aluminosilicates, complemented by ^{29}Si NMR spectra, showed that the concentration of negative charge, now in the form of Al–O–Al linkages, is favored by higher field-strength cations (as for the distribution of Q^n species in Al-free silicates) [5]. Thermodynamic modeling of the effects of Al/Si ratio on speciation predicted heats of reactions that are consistent with solution

calorimetry and that were, for a few compositions, confirmed by observed increases in Al/Si disorder in glasses with higher fictive temperatures, making a larger contribution to configurational heat capacity. Subsequent extensive work on high-pressure aluminosilicates has begun to elucidate the much more complex linkages among not only tetrahedral network species but five- and six-coordinated Al and Si, where the mixing of all of these network species presumably contributes to increases in configurational entropy [16].

The same experimental approach can, in some borosilicate glass compositions, quantify the extent of mixing of boron and silicon network cations, which can be much greater than considered in early models based primarily on ^{11}B NMR data (Figure 3). In compositions with modifier oxides, the structure is further complicated by the presence of both BO_3 and BO_4 groups. As for aluminosilicates, relatively highly charged B–O–B linkages between two of the latter seem to be at least partially “avoided.” When pairs of network cations are present that can have strong nuclear dipolar couplings, notably ^{11}B and ^{27}Al , or ^{27}Al and ^{31}P , double-resonance NMR methods can reveal their relative proximities and even the correlations of species with multiple coordination environments, for example of BO_3 groups with AlO_4 [17]. These findings again can provide important constraints on mixing and contributions to order/disorder.

8 Perspectives

Technical advances continue to increase the quality, depth, and breadth of information that can be obtained about short-range structure and order in oxide glasses, for example, microscale XAS, X-ray Raman, improved

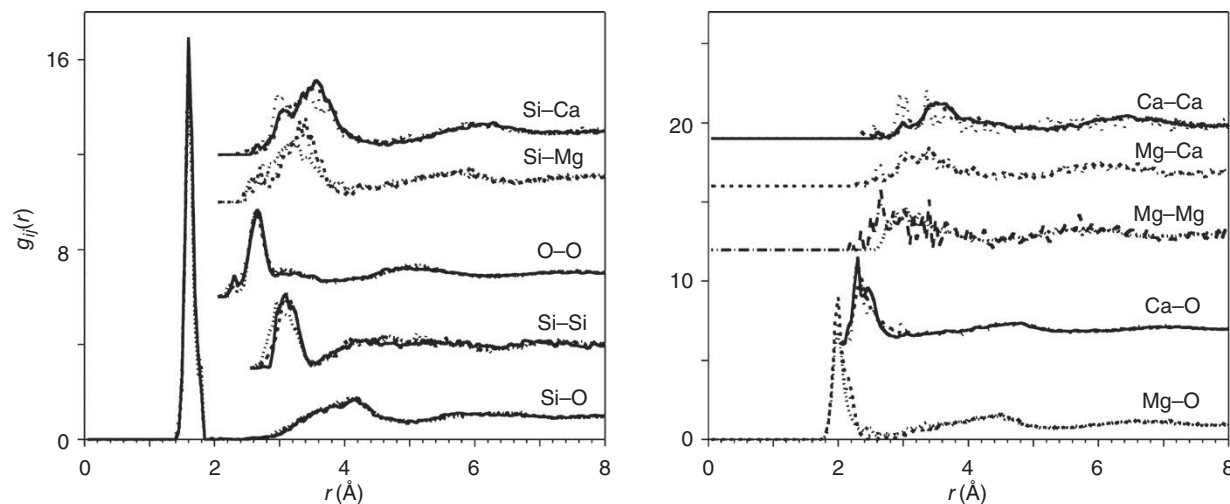


Figure 7 Partial pair distribution functions $g_{ij}(r)$ calculated from a “reverse Monte Carlo” model combining X-ray and neutron diffraction data for various CaSiO_3 – MgSiO_3 glasses. Source: Reprinted with permission from [18].

neutron scattering facilities, and NMR at higher magnetic fields and with methods that allow better measurements of internuclear distances and connectivities. Combination of experimental data from different methods, to yield consistent models, is especially powerful, as illustrated in Figure 7 [18]. Some of these approaches are now feasible for in-situ studies of high-temperature liquids and even of liquids at high pressure and temperature. Advances in theory are beginning to allow accurate forward calculation of spectra (e.g. vibrational and NMR) from structural models [19]. This information can then be combined with experimental data to obtain much more complete views of structure, quantitative extent of disorder, and their links to thermodynamic properties that depend critically on configurational entropy, such as viscosity, heat capacity, and the bulk free energy. As researchers move beyond model-dependent fitting and interpretation of spectra of glasses to more complete theoretical analyses, our understanding of the true complexities of these fascinating and useful materials will expand enormously.

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2.5

The Extended Structure of Glass

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1 Introduction

The structure of glass stretches from atomic dimensions and local short-range order (SRO), which is often similar to that of the crystalline state, through intermediate-range order (IRO) and long-range order (LRO) on the nano-scale, which has no parallel in periodic materials. Sometimes IRO and LRO are grouped together as medium-range order (MRO). Glasses have a monolithic structure, which in principle can extend indefinitely from the atomic scale, via the mesoscale to macroscopic dimensions. The extended structure of glass even encompasses the thousands of square meters emerging from the float process, the quenched field of volcanic obsidian, the kilometers of optical fiber, or the reels of metallic glass tape. Contrary to received wisdom, glasses are in general practically defect-free relative to crystalline materials. The fraction of broken bonds in fiber-quality silica, for instance, is a few parts per million. In generating the macroscale, the self-similar configurations of SRO extend virtually continuously everywhere.

The extended structures of glasses generally define their functionality. In silicate and aluminosilicate glasses, for example, tetrahedral bonding through corner-sharing oxygens ensures that the gap between the occupied oxygen p states and unoccupied antibonding sp^3 levels is retained everywhere (this is the so-called HOMO–LUMO gap between the highest occupied and lowest unoccupied molecular orbitals). The existence of relatively few mid-gap defect states in turn guarantees visible and UV transparency for windows, optical components, laser glasses, etc. In metallic glasses, the cohesive potential between the delocalized electron gas and the ion cores

is maintained isotropically throughout the bulk. These features underwrite electrical conductivity and, without the dislocations of crystalline metals, extremely high levels of mechanical hardness and toughness. Likewise, the spin–spin exchange interaction is retained in aperiodic metallic structures, supporting the ferromagnetism exploited in low-loss magnetic metallic glass-transformer cores. Additionally, because most glass formers – either metallic or not – derive from reasonably strong liquids, they have a wide supercooled liquid range and exhibit superplasticity at the softening point (10^8 Pa·s) but virtual rigidity at the glass transition (10^{12} Pa·s). Through Newtonian viscous flow, their monolithic structures enable the easy fabrication of components with essentially any shape, from the industrial dimensions of windscreens down to those of MEMS and nanotechnology.

By contrast, in crystalline materials even the largest industrial single crystals are extremely small by comparison to glass sheet. Large-area crystalline films comprise micron-sized powders such that the facets of polycrystals generate a microstructure of interlacing grain boundaries where functionality generally resides. For example, the ductility of metals, the hardness of ceramics, the strength of steels, and the mesoscale magnetism of metal films mainly derive from the properties of grain boundaries that are often structurally disordered and anisotropic. By comparison glasses are structurally isotropic, and the cracks that affect their mechanical strength are usually restricted to the surface where the atomic structure terminates. The extended structure of glass links the SRO of atoms, molecules, and metallic clusters and geometrically underpins its intrinsic isotropic properties – optical, electronic, dielectric, electrolytic, magnetic, mechanical, etc. This can be visualized through computer-simulated structures (Figure 1), where the open network of a silicate glass is contrasted with the dense close-packed arrangement of a metallic glass.

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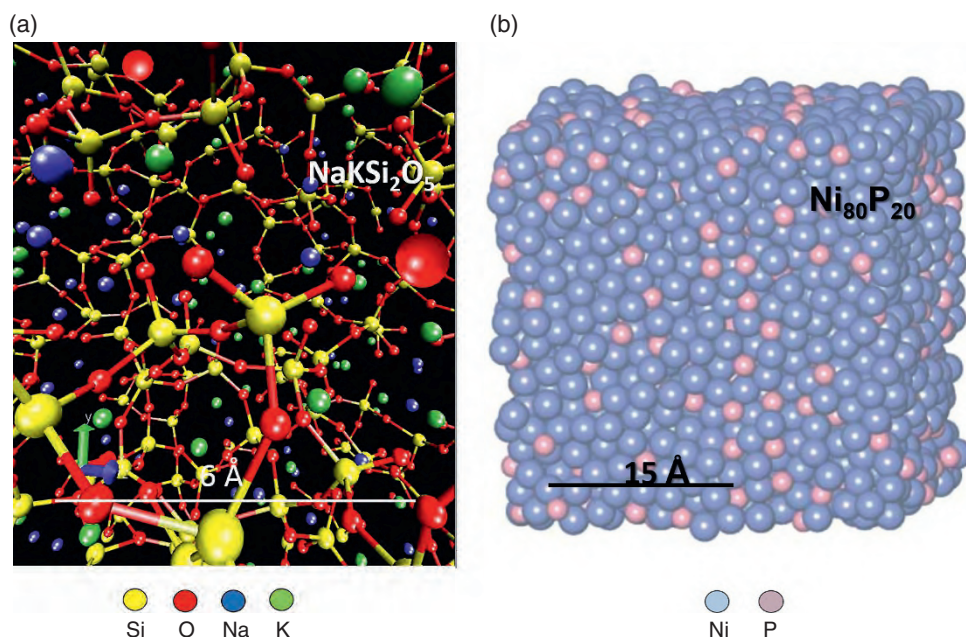


Figure 1 Visualizing the extended atomic structure characteristic of glass. (a) Molecular dynamics simulation of the network structure of NaKSi₂O₅ glass [1, 2]; Na and K atoms are dispersed within depolymerized silicate network, forming percolating alkali channels. (b) Reverse Monte Carlo simulation of the close-packed structure of the metal-metalloid glass Ni₈₀P₂₀ [3, 4]; P atoms also cluster, forming percolating channels through the Ni dense random packed structure. The scale bars indicate the start of long range order (LRO). Source: (b) Reproduced from [4] © 2006 Nature Publications.

The respective atomic volumes are 7 and 11 Å³ and are typical of these very different families of glass, but where each share an extended defect-free structure. Reviews of network glasses and metallic glasses can be found in [1, 3], respectively.

In this chapter we consider how several experimental techniques are required to access the extended structure of glass (Section 2), from diffraction and inelastic spectroscopies that reveal relationships between SRO, IRO, and LRO structure and dynamics, to microscopy that probes the average projected structure in real space. We then turn to the different types of structural order that characterize network and metallic glasses (Section 3): starting with the SRO, progressing through the configurations of adjacent local structural units that define IRO, and extending through MRO to LRO, the topology of larger agglomerations – clusters, rings, channels, and chains. Beyond these dimensions are those of density fluctuations (DFs) (Section 4), frozen into glasses from the liquid state, which reflect the degree of non-ergodicity frozen in at the glass transition. In particular, DFs are the agents at super-cooled temperatures that promote phase separation, either in density or in composition. Models of extended glass structure (Section 5) are next described and include conceptual models, devised before the advent of computational methods but still useful heuristically, and large computerized models that have been developed since.

Using this approach, we show how structural heterogeneity in glasses (Section 6) can be modeled in terms of minority-component channels percolating through the majority network or metallic structure. Here, as elsewhere, the extended structure of glass is linked with its applications. Finally, we outline perspectives for future work (Section 7).

Acronyms

AFM	atomic force microscopy
BO	bridging oxygens
BP	boson peak
CN	coordination number
CRN	continuous random network
DAS	dynamic-angle spinning nuclear magnetic resonance
NMR	density fluctuations
DF	density functional theory
DFT	density fluctuations
DRPHS	dense random packing of hard spheres
EXAFS	extended X-ray absorption fine structure
HR TEM	high-resolution transmission electron microscopy
INS	inelastic neutron scattering
IXS	inelastic X-ray scattering
IRO	intermediate-range order

LRO	long-range order
MAS	magic angle spinning nuclear magnetic
NMR	resonance
MD	molecular dynamics
MRO	medium-range order
MRN	modified random network
NBED	nanobeam electron diffraction
NBO	nonbridging oxygens
PSG	phase-separated glasses
RMC	reverse Monte Carlo
SRO	short-range order
VDOS	vibrational density of states

2 Extended Structure of Glass: The Need for a Multiplicity of Techniques

In addressing the extended structure of glasses, a wide portfolio of techniques has developed [1, 3, 5]. For many years the principal experimental method has been X-ray and neutron scattering [6], initially concentrating on the radial distribution function (RDF) from which the radially averaged local structure $T(r)$ can be determined, as illustrated in Figure 2 for silica glass and the metallic glass $\text{Ca}_{60}\text{Mg}_{25}\text{Cu}_{15}$. The maxima identify interatomic correlations, first between nearest neighbors (SRO) defining the polyhedral or icosahedral building units and then between adjacent units (MRO or IRO), as spelt out in the cartoons. The SRO and IRO in glasses are often similar to their crystalline cousins. On the other hand, topology influences LRO – ring statistics for network glasses [1] and icosahedral packing for metallic glasses ([3], Chapter 7.10) – where mismatching frustrates crystallization.

Attention has subsequently shifted to the measured scattered intensity $i(Q)$ from which the static structure factor $S(Q)$ is obtained, which leads to $T(r)$ via Fourier transform [1]. The scattering vector Q is defined by $Q = 4\pi\sin\theta/\lambda$, where θ is the scattering angle and λ the wavelength of the scattering particles. The $i(Q)$ for the two exemplar glasses are plotted in Figure 3. Two important features are located early on for $Q < 5 \text{ \AA}^{-1}$: the first sharp diffraction peak (FSDP), for which the spacing $2\pi/Q_{\text{FSDP}}$ is a metric for IRO, and the principal peak (PP), which is directly related to the average nearest-neighbor distance $2\pi/Q_{\text{PP}}$ [6, 7]. Both the FSDP and the PP are features common to network glasses as well as metallic glasses (Figure 3). With high-intensity spallation neutron sources, the Q -range reliably reaches $50 \text{ \AA}^{-1}$, enabling the $T(r)$ to be confidently measured to $20 \text{ \AA}$, embracing SRO with LRO.

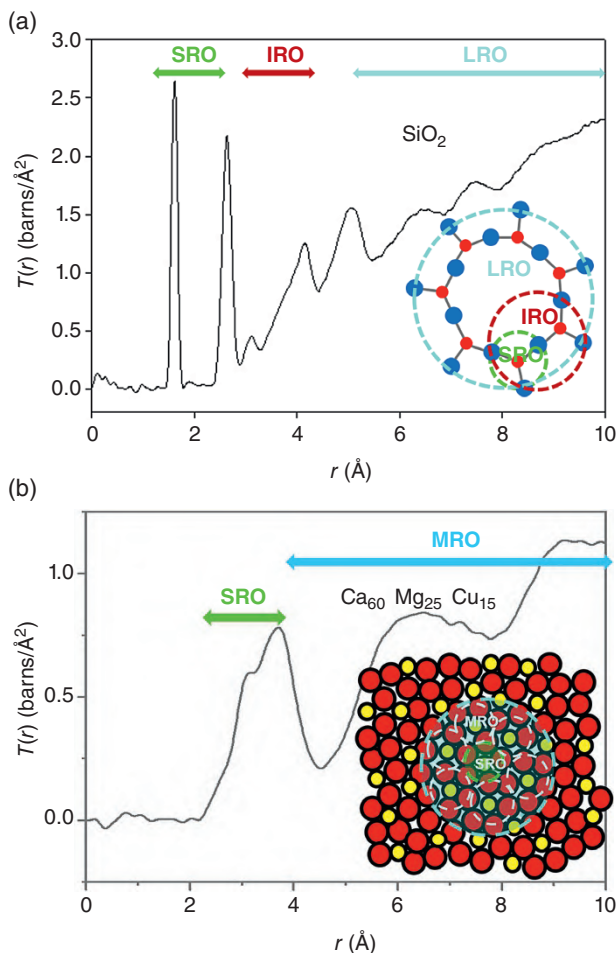


Figure 2 Contrast between the radially averaged local structure $T(r)$ of directionally and metallically bonded structures as exemplified by the network glass SiO_2 (a) and the bulk metallic glass $\text{Ca}_{60}\text{Mg}_{25}\text{Cu}_{15}$ (b). The short (SRO), intermediate (IRO), long (LRO), and medium (MRO) range orders are identified alongside 2-D schematics of local atomic arrangements. Note the difference in the widths of atomic shells reflecting the bonding strength of covalent networks compared to the dense metallic random packings. Source: Courtesy of A. Hannon (<http://alexhannon.co.uk/DBindex.htm>).

Compared with diffraction techniques used for crystalline materials, diffuse scattering methods seriously underestimate the extended structure of glass, even for monatomic systems. Other independent structural measurements are needed in order to increase the credibility of atomistic models. Although X-ray and neutron $S(Q)$'s are independent measures of the same radially averaged structure, until recently X-ray measurements lacked the extensive Q -range of neutron instruments. However, with the arrival of high-energy X-ray scattering [8], both methods are now compatible and are generally applied sequentially to the same material.

Most glasses, though, are multicomponent, which adds chemical complexity to the radial averaging of

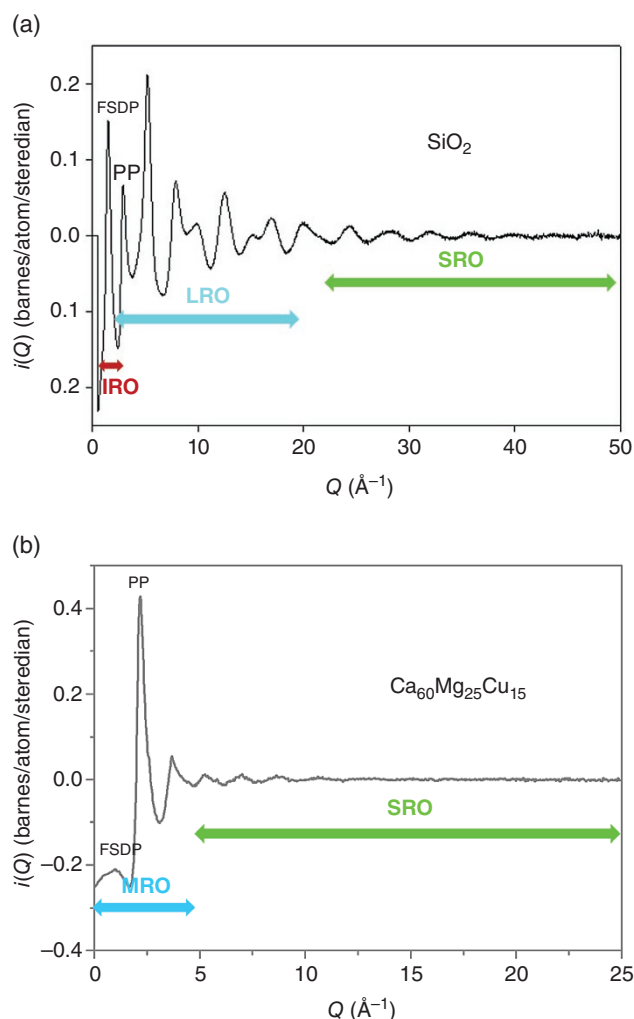


Figure 3 Contrast between the network structure of SiO_2 (a) and the metallic structure of $\text{Ca}_{60}\text{Mg}_{25}\text{Cu}_{15}$ (b) manifest in the scattered intensities $i(Q)$, from which the $T(r)$'s of Figure 2 were obtained. The SRO as defined by the principal peak (PP) and IRO defined by the first sharp diffraction peak (FSDP) are labeled alongside LRO and MRO for each glass. Source: Data courtesy of A. Hannon (<http://alexhannon.co.uk/DBindex.htm>).

three-dimensional (3-D) arrays. More chemically selective techniques are thus generally required, even though isotopic neutron scattering can assist when different isotopes of an element are available [6]. Accordingly, neutron and X-ray scattering are now increasingly complemented by spectroscopies, like magic- and dynamic-angle spinning nuclear magnetic resonance (MAS NMR and DAS NMR), and extended X-ray absorption fine structure (EXAFS) [1, 5, 9]. As these are element specific and increase the mix of independent measurements of the same structure, they add rigor to models of extended glass structure derived from computational methods such as reverse Monte Carlo (RMC) and molecular dynamics

(MD) [1, 10–12]. Moreover, expressed as $S(Q)$, the credibility of predictions of atomic arrangements in glasses can be judged against experimental data quality.

Compared to the direct analysis of experimental RDFs, which dates back to the 1930s, these new combinations of experiment and computational modeling now offer impressive insight into the nature of the extended structure glasses, on the scale of 30 $\text{\AA}$ or more (Figure 1). Often glasses with equivalent local structure lead to images that at first glance appear to be quite dissimilar (Figure 4). The tetrahedral glass network of silica may thus be contrasted with that of amorphous ZIF-8 – one of a newly discovered family of hybrid glasses derived from organic–inorganic materials [14, 15]. The extended structure of silica is perpetuated through corner-sharing SiO_4 tetrahedra (SRO) via bridging oxygens (BOs), IRO ultimately extending to LRO comprising rings of different size (Figure 4). The geometry of amorphous ZIF-8 [$\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2$] develops in a similar way, with Zn atoms tetrahedrally coordinated to 2-methylimidazolate bridges that form into silica-like rings, despite the atomic volume being hugely different, viz. the $11.1 \text{ \AA}^3$ of SiO_2 compared with the $73.4 \text{ \AA}^3$ of amorphous $\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2$.

In adding further confidence to modeling extended glass structure, studies of dynamic properties, using inelastic spectroscopies like inelastic neutron scattering (INS) and Raman spectroscopy, have played an important part [1, 5, 16] – principally in highlighting stretching and bending optic mode vibrations between the atom pairs in network glasses and providing fingerprints of the polyhedra and small molecular groups that constitute SRO and aspects of IRO.

At lower frequencies, inelastic spectroscopies like INS access acoustic modes that are generically subsumed into the boson peak, ubiquitous in the glassy state [1, 5, 17–19]. Derived from the localized collective vibrations of groups of atoms, the boson peak relates to the dynamics of MRO and LRO considered to be the source of fast β relaxation [1, 7]. Located at the bottom of the vibrational density of states (VDOS) in the THz region (1 THz = 4.1 meV), the boson peak is generally accepted as comprising quasi-localized transverse vibrational modes (Chapter 3.4 [16, 18]). These vibrations also enhance the specific heat C_p at low temperatures above the Debye threshold – typically around 10 K. Using either INS or excess C_p reveals that the boson peak intensity is directly related to glass density (Figure 5a–d [18, 19]). For zeolites, which share compositions with silicate and aluminosilicates but have characteristically low densities, the different cage-like units that define their nanoporous structures resonate at different THz frequencies [16]. As the temperature or pressure is increased, these subunits collapse [1] through a process of decelerated melting [21], and a glass, similar in density to a melt-quenched glass, is formed

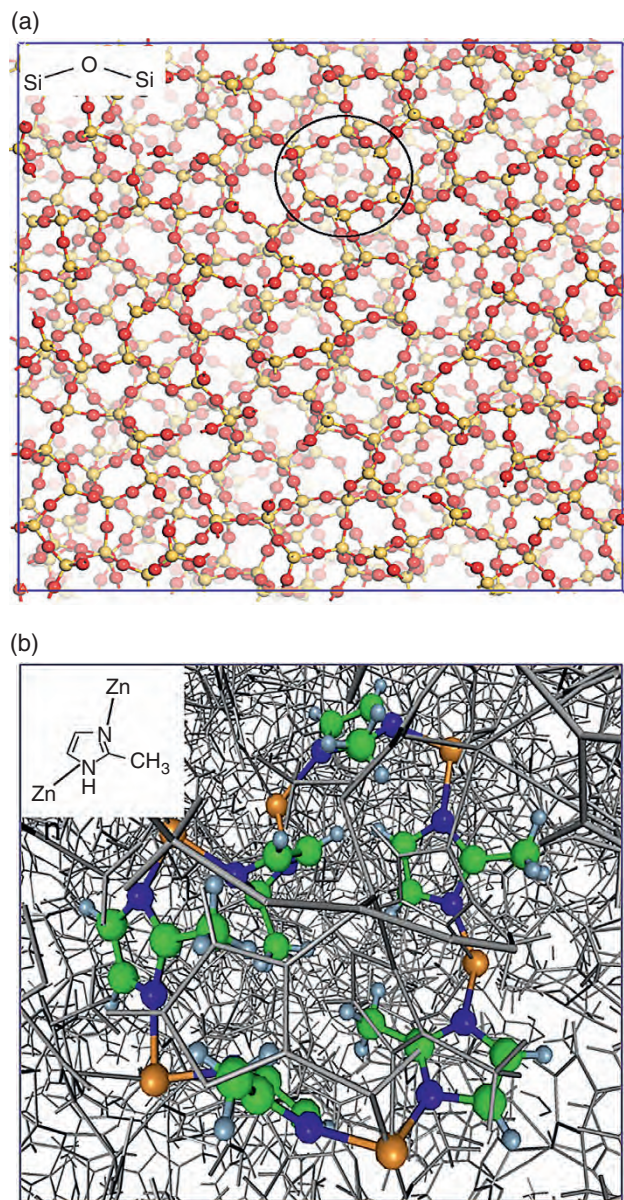


Figure 4 Visualization of MD simulations of two tetrahedral glasses with vastly different atomic volumes but both conforming to the CRN prescription [13]. (a) SiO_2 glass ($11.1 \text{ \AA}^3$). (b) Hybrid glass ZIF-8 ($\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2$) ($73.4 \text{ \AA}^3$). Source: Images courtesy of J. Du (a) and W. Chen (b).

with a single boson peak (Figure 5e). In particular, atomic volume and peak intensity I_{BP} are correlated, with the peak frequency ν_{BP} shifting to higher values as the atomic volume falls.

As for metallic glasses (Chapter 7.10), these also exhibit soft collective vibrations whose origins are similar to oxide glasses boson peaks [3, 20]. If these are accessed from low-temperature C_p experiments, then the enthalpy captured at supercooled temperatures can also be recorded. A direct link exists between I_{BP} and the glass

enthalpy, which can be reduced by annealing Figure 5f [20]. As annealing increases, the glass density, ν_{BP} , also increases while I_{BP} decreases (compare Figure 5e and f).

Whereas inelastic scattering $S(\omega)$ measures the VDOS integrated over Q , and the structure factor $S(Q)$ time-averaged atomic distributions, both derive from the dynamic structure factor $S(Q, \omega)$, which through comparisons with experiment affords a global view of the structure and dynamics of glassy systems and melts over extended regions of space and time. Related to $S(Q, \omega)$ is the intermediate scattering function $F(Q, t)$, which registers structural relaxation from liquid to glass as a function of time [1]. In the limit $t \rightarrow \infty$ $F(Q, t)/S(Q)$ yields the non-ergodicity factor $f(Q, T)$, which is particularly relevant in the present context as it records the degree to which a liquid departs from thermodynamic equilibrium as it is supercooled (Section 4.1). It is readily measured using inelastic X-ray scattering (IXS). Structural relaxation is dominated by fast β processes at high temperatures, with slow α processes emerging through the supercooled region, only to be frozen out at the glass transition T_g .

Microscopy has always played a part in glass structure determination, albeit as a distant companion to diffraction and spectroscopy techniques. It originally provided qualitative evidence for IRO [7]. But the SRO and LRO of network glasses can now be imaged [1, 22] with the emergence of atomic-scale resolution by atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM). With nanobeam electron diffraction (NBED), images can also be obtained for the variety of icosahedral clusters present in metallic glasses [23] (Figure 6).

3 Structural Order over Different Length Scales

3.1 Network Glasses

Network-oxide glass formers like SiO_2 , GeO_2 , P_2O_5 , and B_2O_3 [1] are defined by three- or fourfold directionally bonded polyhedra comprising hybridized units measuring $\sim 2.5 \text{ \AA}$, similar to nearest-neighbor arrangements in crystalline polymorphs [1]. For low-density hybrid glasses like a-ZIF-4 and a-ZIF-8, tetrahedral units are much larger, measuring about $9.5 \text{ \AA}$ [14]. Generally, SRO polyhedra are comparatively rigid, with variations in bond angle of less than 10%. The IRO is located between 3 and $4 \text{ \AA}$ for oxides increasing to $13 \text{ \AA}$ for hybrid glasses, covering correlation distances between SRO polyhedra (Figure 2 [1, 7, 14]). In oxide glasses the interpolyhedral distance is defined by the BO that is also hybridized, with interpolyhedral angles ranging from around 145° for SiO_2 , 130° for

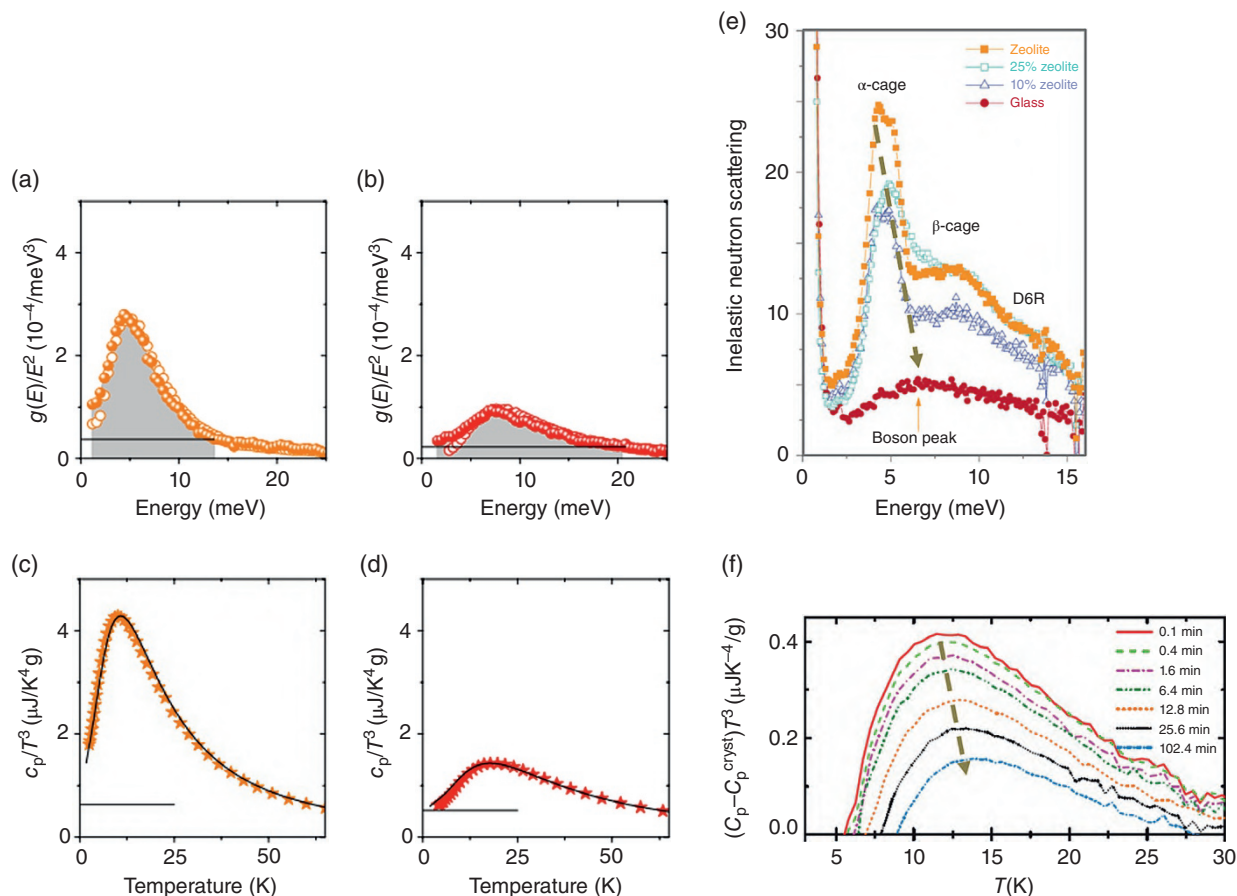


Figure 5 The collective atomic vibrations involved in the boson peak observed either dynamically in the reduced density of states $g(E)/E^2$ (a, b) or thermodynamically in the non-Debye excess low-temperature specific heat C_p/T^3 (c, d) for silica (left) and densified silica (right). Similar features occur in crystalline SiO_2 isomorphs of similar density [18]. (e) INS spectra of the collapse of zeolite Y [16], the cage subunits merging into a single peak of lower intensity I_{BP} as a glass is formed while ν_{BP} increases – dashed arrow. (f) Boson peak in the metallic glass $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ [20] where annealing increases the density, but decreases the trapped enthalpy and the C_p/T^3 intensity I_{BP} falls as ν_{BP} increases – dashed arrow. Source: (a–d) Reproduced from [18] © (2014) APS; (e) reproduced from [16] © (2005) AAAS; (f) reproduced from [20] © AIP.

GeO_2 , and P_2O_5 to 120° for B_2O_3 (Figures 1 and 4 [1]). The imidazolate bridge between metal nodes in a-ZIFs is $\sim 145^\circ$ [14]. On average, the rigidity of tetrahedral and bridging angles is similar.

In network glasses LRO begins at around $6 \text{ \AA}$ – the width of a typical sixfold ring (Figures 1 and 4) – and continues as far as out as features in the RDF can be discerned (Figure 2). Providing a direct link with a multiplicity of rings of corner-sharing polyhedra with different sizes, LRO is perpetuated through modest variations in bond angles, as illustrated in Figure 6 with the two-dimensional (2-D) distributions directly observed for silica [1, 22]. Combinations of experimental RDFs with computer simulations afford 3-D models of network topology where rings are often puckered in conformations foreign to crystalline geometries through variation and twisting of dihedral angles (Figures 1 and 4). The network statistics in SiO_2 glass include five-, six-, and sevenfold rings, as illustrated schematically in Figure 7, in contrast to the

sixfold ring topology of crystalline silicates. In addition, three- and fourfold rings are also found, but in much smaller proportions [1, 6]. They have been identified with the oxygen “defects” that give rise to breathing modes in Raman spectra [1]. These miniature rings increase in number when pressure is applied, for example, in indentation experiments. The converse applies in B_2O_3 glass where the network is less 3-D than in SiO_2 and where Raman spectra are instead dominated by the threefold boroxol ring feature [1]. Pressure causes boroxol rings to break up into buckled ribbons, the dimensionality decreasing further.

Another consequence of LRO in network glasses is the quasiperiodic alignment of groups of caged voids associated with the aperiodic network of rings (Figure 7) to which the FSDP at Q_{FSDP} (Figure 2) is attributed [7]. In glass formers like SiO_2 and B_2O_3 , $2\pi/Q_{\text{FSDP}}$ distances lie around $4 \text{ \AA}$. In chalcogenide glasses, such as As_2S_3 and GeSe_2 , SRO polyhedra are larger ($\sim 4 \text{ \AA}$), leading to

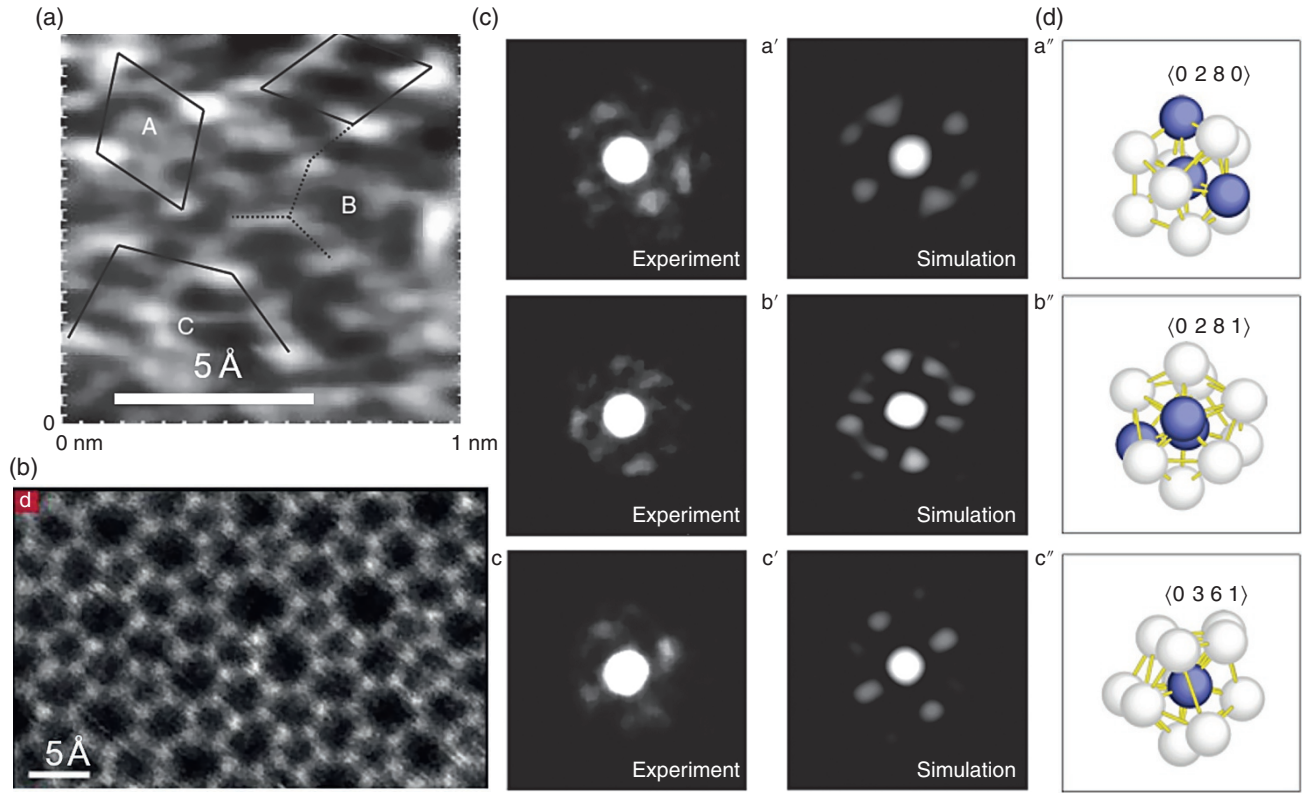


Figure 6 Direct observation of the atomic structures of glasses. (a) Atomic force microscopy image from freshly fractured silica in ultra-high vacuum, revealing a 2-D projection of the near-surface structure and showing SRO and fragments of rings – solid and dotted lines – contributing to LRO [24]. (b) Atomic resolution transmission electron microscope image of a graphene-supported silica bilayer, showing SRO and extensive LRO network with a variety of ring structures [22], consistent with Zachariasen’s CRN [13] (Figure 7a). (c) Nanobeam electron diffraction patterns of $Zr_{0.667}Ni_{0.333}$ metallic glass [23] (left), with their simulated patterns (right) in terms of the icosohedra shown in (d). The different SRO reflect the variety of icosohedra in Bernal’s DRPHS model of liquid metals [25] (Figure 7b). *Source:* (a) Reproduced from [24] © (2004) Elsevier; (b) reproduced from [22] © (2012) ACS; (c, d) reproduced from [23] © Nature Publications.

larger quasiperiodic void separations (~ 6 Å). In all cases FSDP distances decrease as pressure is applied but also become more dispersed, the FSDP peak widening and decreasing in intensity with increasing glass density [7].

Importantly these changes in the FSDP properties of network glasses with pressure correlate with those of the boson peak [17], where ν_{BP} increases and I_{BP} decreases with increasing pressure and therefore density, supporting the view that the BP comprises collective atomic motion of large groups of atoms whose breathing frequency increases as their size shrinks. Furthermore, excess C_p in glasses is attributed to a double-well vibrational potential, which, in silica, can be modeled through the librational twisting of pairs of tetrahedral units, underscoring how the dynamics of IRO promote buckling of rings across LRO in network structures.

3.2 Metallic Glasses

In metallic glasses (Chapter 7.10) bonding is directionless and SRO comprises clusters of atoms around 3 Å in

diameter [11, 12]. Coordination numbers (CN) are between 10 and 11 – much greater than in directionally bonded glasses. With respect to crystalline metals, the CNs of metallic glasses exceed 8, the value for bcc structure (8), but fall short of 10, the CNs for fcc and hcp structures. Atomic cluster units in metallic glasses are around 5 Å apart, similar to interpolyhedral IRO distances in network glasses. The interatomic correlations between neighboring cluster units are identifiable out to around 15 Å (Figure 2), similar to the establishment of LRO in network glasses. In these densely packed metallic structures, however, the geometry of bond angles and dihedral angles and ring topology is absent. The sequence from IRO to LRO is usually collectively described as MRO [4], but is less well understood than in network glasses.

Furthermore, compared to supercooled network systems, where high shear viscosity and low atomic diffusion stem from the existence of open structures, the glass-forming ability of densely packed metallic melts is imprecisely understood. In searching for melt compositions that are suitably viscous for conventional glass

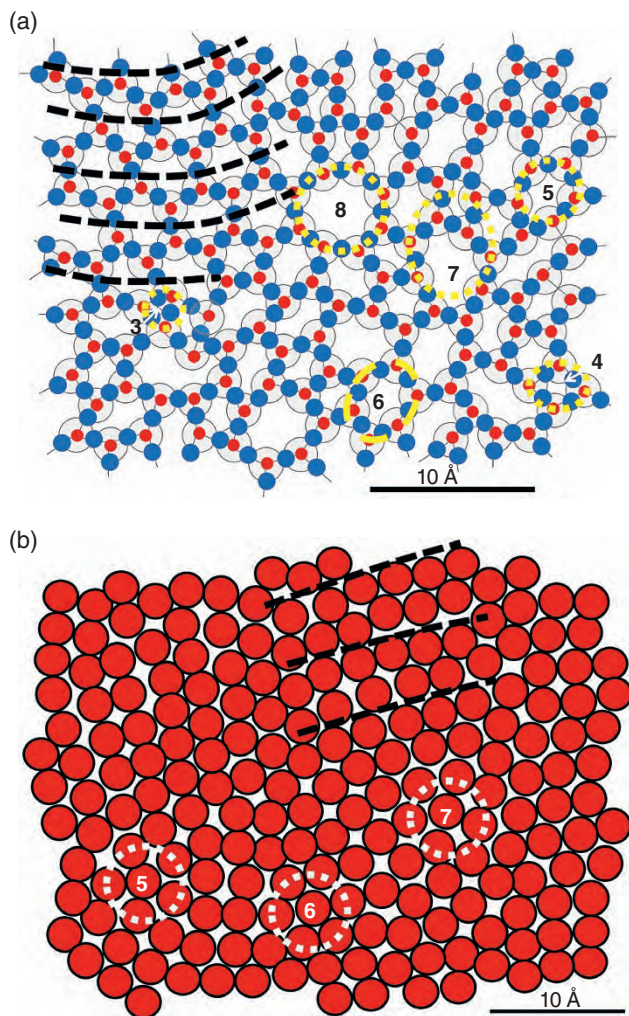


Figure 7 Simple two-dimensional models of glass structure created from sparse (a) and dense (b) packing of spheres. (a) The continuous random network (CRN) model of Zachariasen [13] representing a network glass comprising threefold coordinated cations and bridging anions. Different ring sizes (3, 4, 5, 6, 7, 8) perpetuating extended range order are shown. (b) The dense random packing of atomic spheres (DRPHS) model of Bernal [25] showing variations in icosahedral packing, viz. 5, 6, and 7, that promote homogeneous noncrystalline extended range order.

quenching, those associated with deep eutectics can be a guide, but not exclusively so [4, 23]. An overriding requirement, though, resides in achieving the highest atomic packing density in the supercooled state, which is often achieved by “dissolving” smaller atoms. The atomic size ratio for solute to solvent atoms, which yields the most efficient packing, is frequently found to be approximately 0.9 [4].

For complicated high-density geometries, different packing arrangements in metallic glasses are now modeled with computer simulations – mainly RMC, but also *ab initio* MD – the aim being to analyze the variety and

number of different Voronoi polyhedra present [23]. For an atomic size ratio of 0.9, SRO is predominantly icosahedral, the geometry for tessellated quasicrystal structures. In glasses with pronounced chemical order and atomic size ratio lower than 0.9, pentagonal bipyramids replace icosahedra as the dominant Voronoi polyhedra. Because they embody fivefold symmetry, icosahedrons and pentagonal bipyramids frustrate crystalline close packing and represent the geometric counterparts to odd-membered rings in directionally bonded glasses with open structures.

Metallic glasses, like network glasses, are less dense than their crystalline counterparts, the additional free volume being a throwback from the configurational diversity of the supercooled liquid. In contrast to that of network glasses, though, the FSDP in metallic glasses (Figure 3) is considered to derive from scattering from voids interspersed within the SRO of atomic clusters (Figure 7). In Ca–Mg–Cu glasses, Q_{FSDP} is, for example, about $1.2 \text{ \AA}^{-1}$, and the FSDP correlation length about $5 \text{ \AA}$ (Figure 3). In multicomponent alloys Q_{FSDP} is affected by the size distribution of the different metals and its intensity by density. In Ni–Zr–Al, Q_{FSDP} is, for example, about $0.9 \text{ \AA}^{-1}$ with a FSDP correlation length of about $7 \text{ \AA}$.

Also found in metallic glasses, the excess THz modes at the onset of the VDOS and linear low-temperature specific heat first observed in oxide glasses at THz frequencies [7] appear to have a common origin in the behavior of collective transverse acoustic modes at the Ioffe–Regel limit, where the phonon mean free path equates with its wavelength [19]. At this point vibrations no longer propagate, which suggests that LRO vibrations are localized. Demonstrated by computer simulation of Lennard-Jones glass models, collective vibrations in these close-packed structures replicate the scaling down of I_{BP} with density referred to earlier and the increase in ν_{BP} .

4 Structural Aspects of Density Fluctuations

4.1 Non-ergodicity and Elastic Moduli

Beyond the length scales of LRO and MRO are the DFs characteristic of the liquid state. They originate from the dynamics of the liquid state in thermodynamic response to temperature and pressure. Whereas liquids are in equilibrium and ergodic above the melting point, supercooled liquids are non-ergodic at T_g , which is reflected in the size of the non-ergodicity factor $f(Q, T)$ (Section 2). In particular $f(Q \rightarrow 0, T)$ is related to the magnitude of DFs, and as $T \rightarrow T_g$, a dynamic crossover occurs to non-ergodicity – typically $\sim 1.2T_g$. On vitrification DFs increase in amplitude and eventually become frozen in.

In glasses the spatial extent and amplitude of DFs can be determined from IXS and $S(0)$ [1]. In glass formers DFs are typically ≥ 20 Å in scale, their amplitude being proportional to the melt compressibility κ , which is greater for network glasses than metallic glasses, for example, reflecting the considerable differences in atomic packing (Figure 7). In network glasses like silica, light scattering from DFs limits losses in fiber-optic applications [7]. Interestingly the amplitude of DFs is inversely related to Poisson's ratio, which is smaller for oxide glasses, which are usually brittle, than for many metallic glasses, which are tough [17].

4.2 Polyamorphism and Phase Separation

At high degrees of supercooling, liquid–liquid phase transitions have been observed, a phenomenon now commonly referred to as polyamorphism ([26], Chapter 3.9). These phase transitions have been observed in water, supercooled oxides, semiconductors, and metallic alloys, leading to new types of glass, such as low- and high-density amorphous phases – LDA and HDA respectively – each differing in density and entropy but sharing the same composition [1, 14, 21, 26].

In some multicomponent supercooled oxide liquids, on the other hand, atomic diffusion can result in the coexistence of liquids with *different* compositions, the analogue of multiple phases in crystalline systems. On cooling these lead to phase-separated glasses (PSG) – the best-known being borosilicates [7]. Pyrex, for example, combines low thermal expansion with high mechanical strength, whereas Vycor glass owes its special open microporous structure to the continuous silicate phase that is left when the borate phase has been leached out.

In summary, the extended structure of glass connects all of the various ordered regions present on different length scales and underpins the diverse global properties of the glassy state.

5 Models of Glass Structure

5.1 Conceptual Models

Two conceptual models have proved very influential over the years in picturing the overarching aperiodic structure of glass. Zachariasen's continuous random network (CRN), devised for oxide glasses, dates from 1932 [13]. In 1960 Bernal introduced the dense random packing of hard spheres (DRPHS) to describe the structure of liquid metals [25], which has been applied widely to glassy metals once these had been discovered. Both constructs of glass structure, for insulators and metals, respectively, came in advance of experimental techniques that have

since illuminated their strengths as well as their shortcomings. The two models are illustrated in Figure 7, reduced to 2-D arrangements. Presented in this way, they reveal a common basis for constructing aperiodic arrays from contiguous spheres. They markedly differ, however, because each sphere touches just three neighbors in the CRN, resulting in a more open network structure than with the DRPHS where the number of neighboring spheres lies between five and seven. Taken together, though, both the CRN and DRPHS noncrystalline schemes yield a lower density than for their crystalline counterparts, and voids are seen to align mimicking the quasiperiodicity attributed to the FSDP (dashed curves in Figure 7). The increased free volume derives from variations in packing. As such, both CRN and DRPHS offer respective snapshots of the glassy state without informing on the quenching process during which the configurational entropy is generated. With the CRN each sphere embodies the SRO surrounding individual atoms: MO_3 units, for example, mimic SiO_4 tetrahedra in silica glass or BO_3 and BO_4 polyhedra in borate glasses (Figure 7).

The SRO units are interconnected to create corner-sharing networks of directionally bonded atoms perpetuating indefinitely, which in addition provides a conceptual representation of the extended structures of network glass formers. Although amorphous semiconductors were not yet discovered in 1932, the CRN is equally applicable to chalcogenide glasses like As_2S_3 and also to elemental semiconductors like amorphous As and Ge [7]. In all cases fixed CNs and bond lengths are prescribed by the tenets of the CRN. Usually these parameters are informed from crystalline structures even though space group symmetry is broken by variations in bond angles. Distortions between SRO units lead to rings of atoms of different sizes (Figure 7), including odd-membered rings seldom found in the crystalline state. Because of the bond angle flexibility of the CRN, point defects, like vacancies and interstitials, can formally be avoided, which is consistent with the observation that optical-quality glass is almost free of point defects.

By contrast Bernal's DRPHS structure is the geometric outcome of the random packing of spheres, originally ball bearings in a can [25], each representing a metal atom (Figure 7). Designed to model elemental liquid metals, the DRPHS became an approximate structure for glassy metallic alloys where components have similar atomic radii, such as $\text{Pd}_{80}\text{Si}_{20}$. Nearest-neighbor distances in densely packed structures scale with metallic radii, but the packing scheme in three dimensions incorporates icosahedral units avoiding dense-packed crystalline arrangements. By analogy with the CRN, Bernal's model is free from dislocations that render crystalline metals prone to mechanical damage, which qualitatively explains the

exceptional toughness of metallic glasses. Moreover, as the main contribution to metallic electrical resistivity at ambient temperature is governed by the scattering of electrons by irregularities in the positions of core ions, the DRPHS supports the greater electrical resistivity of glassy metals compared to than crystalline metals, enabling the low-loss of *metglas* magnetic transformer cores.

The major success of the Zachariasen and Bernal models has been in reconciling SRO with the extended structure of the glassy state. These model structures are isotropic and homogeneous by definition, however, and as such they fail to account for DFs observed almost universally in network as well as in metallic glasses. The solution to this drawback can only be solved through the computer modeling of large 3-D melt-quenched structures.

5.2 Computational Modeling of Extended Structure

Atomistic modeling of liquids and solids goes back over 50 years. Over the interim period three main approaches have been developed in relation to glass-forming materials (Chapters 2.7 and 2.8): (i) MD, where empirical potentials describing the repulsive and attractive interactions between atoms are used in conjunction with classical dynamics to explore P–T phase space; (ii) RMC, in which sequential adjustments in atomic positions are made to improve agreement with the experimental structure factor $S(Q)$; and (iii) density functional theory (DFT) based on all-electron quantum mechanical methods that replace the empirical potential in MD. At the present time ensembles 300 Å in size are feasible with MD and RMC, whereas *ab initio* DFT MD, which is computationally more demanding, is currently limited to systems of about 15 Å. Empirical 2- and 3-body potentials are formally ionic but have been successful for predicting the structure and dynamics of liquids and glasses where chemical bonding is predominantly directional in character such as in feldspar compositions ([27], Figure 8). Interestingly, RMC and latterly DFT have been used for metallically bonded systems as well ([4] Figure 1).

Neutron $S(Q)$ data from single experiments were originally used with RMC, together with simple constraints, such as nearest interatomic approach, CN, etc., to avoid unphysical SRO [10]. Now other sources of data are used in conjunction, the most common being high-energy X-ray diffraction [8], but these have been augmented by other sources of data – notably EXAFS and MAS NMR spectra [10]. From large models, LRO effects such as clustering, channels, and other sources of heterogeneity can be examined.

In simulating glass structure with MD and DFT, crystalline ensembles are typically “melted” at, say, 5000 K over 10’s of ps until thermodynamic equilibrium is reached, after which they are cooled at ~1 K/ps, through the supercooled regime and glass transition, to a glass at ambient temperature. At each stage the SRO of bond lengths and bond angles of polyhedra in directionally bonded systems, and bond lengths and icosahedral geometry in metallic systems, can be catalogued and compared with experiment. Likewise, one can examine directly IRO and LRO such as ring statistics in covalent structures and MRO, for example, the icosahedral variety, in metallic alloyed structures. Moreover, dynamic properties like ion diffusivities can be predicted as a function of temperature and pressure, the same applying to vibrational modes that determine the VDOS – not least the many-atom cooperative motion responsible for the boson peak.

6 Structural Heterogeneity in Glasses

The conceptual CRN and DRPHS models for glass structure [15, 16] are based on single-type polyhedra or atoms, respectively, and predict extended range order to be homogeneous everywhere. Because these models are constructed statically, not dynamically, DFs are also excluded. A geometric consequence of introducing more than one size of polyhedron or atom type is *microsegregation* in the packing of the minority component, first as clusters, which then coalesce into channels above the percolation limit (~20%). This evolution was originally predicted from the 2-D modified random network (MRN) model [9] and later from 3-D MD simulated structures [2].

Interestingly, a similar clustering is also evident in computer-simulated metallic glass structures, such as the metalloid P in the RMC model for $\text{Ni}_{0.8}\text{P}_{0.2}$ metallic glass, where this microsegregation can be seen threading through the close-packed Ni structure ([12] Figure 1).

For MRN structures (Figure 8), channels are defined by nonbridging oxygens (NBOs) resulting in silicons, for example, being surrounded by mixtures of BOs and NBOs, which can be readily identified by ^{29}Si MAS NMR [1, 28]. In aluminosilicate glasses, aluminums occupy tetrahedral sites AlO_4^{-1} [1] where the extra charge is compensated for by adjacent modifier cations like alkalis or alkaline earths. For fully compensated compositions, like those of feldspars, glasses, silicon, and aluminum tetrahedra are corner-shared via BOs, adopting a CRN-like geometry that is categorized as a compensated continuous random network (CCRN) [28]. Alkali channels have also been predicted in aluminosilicate melts and glasses, like the nepheline family ($\text{Na}_x\text{K}_{1-x}\text{AlSiO}_4$)

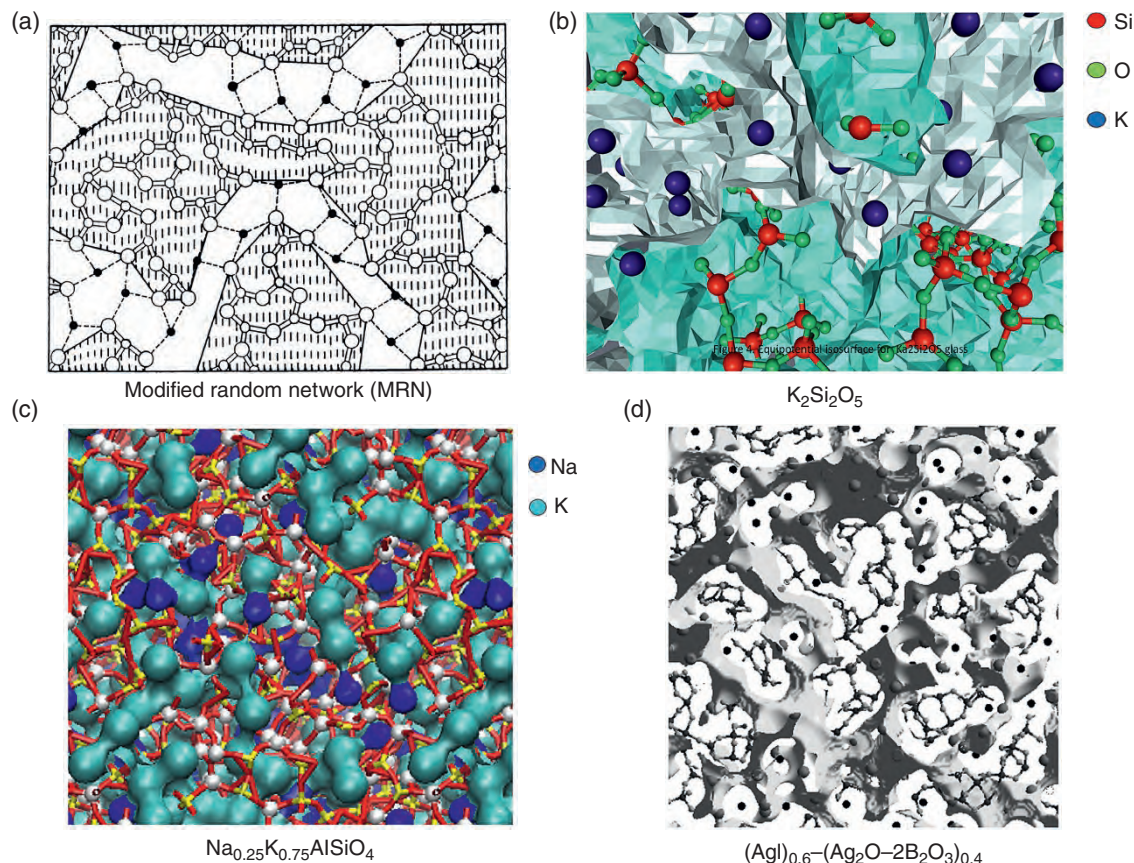


Figure 8 Microsegregation in network glasses. (a) Modified random network (MRN) used to model oxide glasses [9]. Cation modifier channels clearly seen percolating through the two-dimensional network, 3-D microsegregation later confirmed with MD methods [2]. (b) Isosurfaces delineating K^+ conducting pathways in MD simulated $K_2Si_2O_5$ disilicate glass, with cutaway showing adjacent interweaving modified silicate network. (c) Alkali channels in MD simulated aluminosilicate $Na_{0.25}K_{0.75}AlSiO_4$ [27]. (d) Ag^+ channels in the superionic glass $(AgI)_{0.6}-(Ag_2O-2B_2O_3)_{0.4}$ separated from anion borohalide pockets. *Source:* (a) Reproduced from [9] © (1985) Elsevier; (b) image courtesy Z. Zhou; (c) reproduced from [27] © (2017) Nature Publications; (d) reproduced from [10] © 2001 Institute of Physics.

(Figure 8), confirmed by MD modeling, which also reproduces the way the viscosity changes with composition [27].

Modifier channels were envisaged from the start as supporting ionic diffusion, such as that of alkali ions migrating through oxide glasses [28]. The use of isosurfaces to delineate channels (Figure 8) helps visualize the separation of mobile ions from the surrounding network. The presence of well-defined channels explains the additional FSDP observed, for example, in modified silicate glasses around $0.8 \text{ \AA}^{-1}$, which can be attributed to correlations between alkalis with a quasiperiodicity of about $8 \text{ \AA}$ [1]. Other evidence comes from EXAFS and MAS NMR experiments.

There is now much support for the idea of reconciling structural heterogeneity with transport properties [28]. For example, the mixed alkali effect, where the mixing of different mobile alkalis in the same glass drastically affects the mobility of both, can be understood in terms of the

segregation of alkalis packing *within* channels, diluting the diffusivity of each ([2], Chapter 4.6). The huge fall in the average ionic mobility with alkali mixing reduces the ionic conductivity of glass and increases its corrosion resistance and other related transport properties [28].

Fast-ion conducting glasses based on silver salts, like AgI dissolved in oxide and sulfide matrices, have unusually high ionic conductivities at ambient temperature, exceeding those of binary alkali silicates and borosilicates by three or four decades, making them attractive as possible electrolytes for solid-state batteries. For these systems RMC modeling has been interpreted in terms of the MRN and the high diffusivity of Ag^+ along percolating channels that are approximately one-dimensional (Figure 8). Like for conventional modified oxide glasses, the FSDP is often structured for fast-ion conducting glasses with Ag–Ag and anion–anion components, the former with a quasiperiodicity approaching $10 \text{ \AA}$. This is illustrated for $(AgI)_{0.6}-(Ag_2O-2B_2O_3)_{0.4}$ glass in

Figure 8 where the topology of ion transport channels can be clearly seen. As the AgI content increases, extending the composition range (and with it the ionic conductivity), the halide component “pushes apart” the remaining network, which also becomes more disordered. The FSDP is dominated by Ag–Ag quasiperiodicity so that this is the feature that correlates with superionic diffusivity within glass-forming compositions [10].

In these examples, structural heterogeneity is manifest both in the IRO related to the FSDP and topologically over LRO and beyond to embody the extended structure of glass.

7 Perspectives

For the future, the ideas about the extended structure of glass, introduced separately in this chapter, need eventually to be consolidated into a holistic description. This is implicit in the conceptual MRN, CRN, and DRPHS models [9, 13, 25] whose fixed geometries are infinitely perpetuated through rings of different sizes and modifier channels for insulating network glasses and through variations in icosahedra for densely packed metallic glasses. Nevertheless, for the last two decades of research, SRO, IRO, and LRO/MRO have been loosely defined in terms of static geometry between basic atomic building units, correlations between adjacent units, and more distant neighbors. This has created demarcations, often based on different experimental techniques, that avoids the central issue. The extended structure of glass should rather be seen as a continuous development from the microscopic atomic level through mesoscopic dimensions to the macroscopic scale relevant to applications.

The challenge in glass science is to associate, in a quantitative way, atomic structure with functionality [1, 3, 7]. In particular, heterogeneity is a common feature of functional glasses but is incompletely understood at the level of static structures. It has its antecedents in the rheology of the supercooled state and the dynamics of the glass transition. Empirical correlations have been reported, often controversially received, between the fragility m of supercooled liquids at the glass transition and solid-state properties such as Poisson’s ratio, between m and I_{BP} , and between m and $f(0,T)$ [1]. Underlying all these relationships is the role played by DFs, which increase in amplitude at the dynamic crossover $\sim 1.2T_g$ [26] and are frozen into the glassy state as α relaxation dynamics slow down. They appear to be central to nucleation processes, whether these are crystallization, phase separation, or polyamorphism. DFs have the dimensions of the acoustic wavelengths of the boson peak, which underscores, again, the cooperative nature of the many-atom

fast β dynamics in the condensation of glasses and their functionality.

Finally, the important technical drivers in meeting the challenge raised by the prospect of understanding the extended structure of glass as a predictor of functionality are the advances in experimental technology. First are those coming from light and particle beams in materials science – spallation neutron sources, coherent X-ray sources, electron nanobeams, and atomic-scale microscopy. These tools have already escalated in intensity and diversity in recent years, increasingly driven by the needs of the biosciences, where similar issues exist in handling complexity and aperiodicity on a grand scale. Second, and as important, are advances in high-performance computing and the visualization of big data sets. Year on year larger and larger simulations are reported, sizes for MD, currently reaching several million atoms, already on a length scale commensurate with DFs. *Ab initio* techniques, which are the most reliable for predicting functionality, necessarily lag behind, but are currently heading toward the thousand atom mark – all of which concurs with the forward thinking of Alder and Wainwright, over 50 years ago, that “the behaviour of systems of many interacting particles cannot, in general, be dealt with theoretically in an exact way [...] Since these difficulties are not conceptual but mathematical, high-speed computers are well-suited to deal with them” [29].

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2.6

Structure of Chemically Complex Silicate Systems

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1 Introduction

Chemically complex silicate glasses and melts include natural magmatic liquids as well as many commercial glasses. Magmatic rocks sometimes also are used for commercial purposes with slight compositional adjustment made to optimize processes or material properties and reduce costs (e.g. rock wool, Chapter 9.3).

Glass families such as boro- and phosphosilicates are specifically dealt with in Chapters 7.6 and 7.9, respectively. The chemically complex glasses and melts considered here are mainly aluminosilicates with Si^{4+} and Al^{3+} as the main network-formers and alkali metals, alkaline earths, and Fe^{2+} the dominant network-modifiers. Their structure, properties, and structure/property relations can be described with the aid of information obtained with compositionally simpler unary, binary, and ternary compositions and composition joins (Figure 1). The principal composition variables are metal oxide/silica, alumina/silica, and types and proportions of metal cations with different electronic properties (see also [1]).

The structural environment changes when pressure during melting is sufficiently high to cause oxygen coordination changes of Al^{3+} and Si^{4+} (≥ 6 GPa). High-pressure data are so limited, however, that a survey will not be very informative and high-pressure industrial processes are virtually nonexistent. Pressure will not, therefore, be discussed here.

2 Glass and Melt Polymerization

The degree of polymerization of the aluminosilicate network affects most glass and melt properties. Melt

polymerization can be expressed as the proportion of nonbridging oxygen (NBO) per tetrahedrally coordinated cations (T), NBO/T . The NBO/T can be calculated from the chemical composition of a glass and melt, provided that types and proportions of network-forming cations are known. Then, $\text{NBO}/\text{T} = (2 \cdot \text{O} - 4 \cdot \text{T})/\text{T}$, where T and O are atomic proportions of tetrahedral cations and oxygen, respectively, and T is given a formal charge of 4 can be readily calculated.

The principal network-formers (tetrahedral cations) in complex glasses and melts are Si^{4+} and Al^{3+} . These will be discussed first.

2.1 SiO_2

In nature, the SiO_2 concentration in some cases can exceed 80 wt % although in the most common magma, basalt, the SiO_2 range is 45–55 wt %. By comparison, most commercial glasses have from 50 to 70 wt % SiO_2 contents (Table 1).

From the relatively small enthalpy, entropy, and volume of fusion (ΔH , ΔS , and ΔV) of crystalline SiO_2 polymorphs (see [2] for review of data), it may be inferred that silica melt and glass retain a three-dimensional structure of interconnected SiO_4 tetrahedra that exist in its crystalline polymorphs (quartz, tridymite, and cristobalite). From vibrational, X-ray, and NMR spectroscopic studies, one also concludes that the SiO_2 glass structure is essentially fully polymerized [3]. Vibrational spectroscopic spectra recorded at temperature above that of the glass transition of silica glass (1208°C) do not reveal significant structural differences between glass and supercooled liquid. There is an asymmetric distribution of intertetrahedral angles, ranging from ~ 120 to 180° (Figure 2) with a maximum between 145 and 155° [4]. A 145 – 155° Si–O–Si angle is that expected in a three-dimensionally interconnected SiO_2 glass structure

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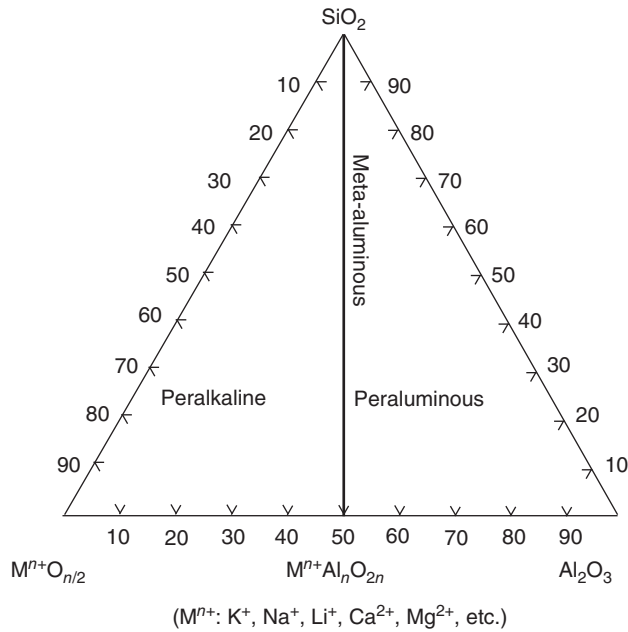


Figure 1 Compositional environment of complex silicate melts and glasses. Peralkaline denotes compositional range where there is excess metal cations (alkali metals + alkaline earths) over that necessary for charge-balance of tetrahedrally coordinated Al^{3+} . Meta-aluminous compositions are those where the proportion of alkali metals + alkaline earths is exactly equal to that needed for charge-balance of tetrahedrally coordinated Al^{3+} . Peraluminous compositions are those where there is excess Al^{3+} over that which can be charge-balanced with alkali metals + alkaline earths.

consisting predominantly of six-membered rings. The somewhat asymmetric Si—O—Si angle distribution (Figure 2) suggests that more than one exists in SiO_2 glass. Rings with three or four SiO_4 tetrahedra coexisting with six-membered rings are those most commonly suggested.

The coexistence of distinct structural units has important consequences because it has been invoked to account for the unusual properties of SiO_2 glass such as a room-temperature density maximum for glass quenched from temperatures near 1505°C . Besides, a density minimum is observed near 950°C for structurally relaxed glass. The anomalous pressure- and temperature-dependence of SiO_2 glass compressibility, with maxima near 3 GPa and 100 K, respectively, can also be modeled with two coexisting three-dimensional structures in SiO_2 glass.

2.2 Al_2O_3

The second most important network-forming component in complex aluminosilicate glasses and melts is Al_2O_3 (Table 1). Its concentration range in most natural magma and commercial applications (5–20 wt % Al_2O_3) can have profound influence on glass and melt properties compared with pure SiO_2 . These include better glass-forming ability of melts, improved durability, lower viscosity, and lower thermal expansion.

The type of metal cations serving to charge-balance tetrahedrally coordinated Al^{3+} is central to understanding the structural roles of Al^{3+} in silicate melts and glasses and, therefore, their physicochemical properties. Charge-balance commonly is achieved with alkali metals and alkaline earths (as in feldspar structures, for example). With an alkali metal, M^+ , one Al^{3+} can be charge-balanced provided that $X_{\text{M}^+} \geq X_{\text{Al}^{3+}}$, whereas for alkaline earths, the requirement is $0.5 X_{\text{M}^{2+}} \geq X_{\text{Al}^{3+}}$, where X_{M^+} , $X_{\text{Al}^{3+}}$, and $X_{\text{M}^{2+}}$ are atomic fractions of the respective cations.

The structural environment near alkalis and alkaline earths depends on whether these ions play a

Table 1 Oxide composition (wt %) of common commercial glasses and glass of common magmatic rocks with additional data from <http://Earthchem.org>.

	Window glass	Pyrex	Glass wool	Rockwool	Rhyolite	Dacite	Andesite	Basalt	Phonolite
SiO_2	72.6	81.1	65	46.6	72.18	65.13	57.51	50.29	56.56
TiO_2				2.4	0.39	0.64	0.93	2.06	0.87
Al_2O_3	0.6	0.43	2.5	13.3	13.23	15.67	16.93	14.79	19.31
B_2O_3		22	4.5						
FeO(T)	0.8	0.2		10.6	2.90	4.73	7.08	10.94	4.02
MnO					0.10	0.82	0.05	0.03	1.05
MgO	3.6	0.3	2.5	9.1	0.48	1.03	1.82	2.5	1.86
CaO	8.7	1.1	8	10	1.53	1.47	1.85	1.38	2.28
Na_2O	14.3	1.5	16.5	5.6	4.03	0.81	0.77	0.55	1.57
K_2O	0.2		0.7	1.4	3.76	0.96	0.86	0.38	1.01
NBO/T	0.79	0.00	0.62	0.99	0.08	0.18	0.36	0.72	0.22

Source: Modified from [1]

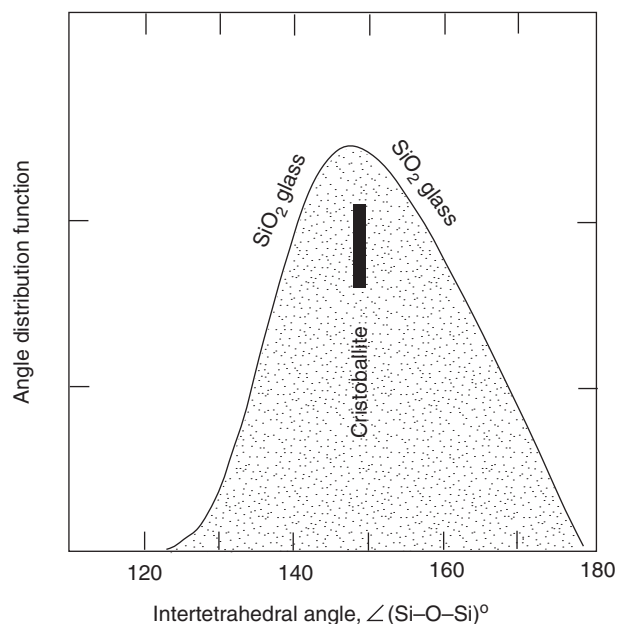


Figure 2 Distribution of intertetrahedral angle, $\angle(\text{Si}-\text{O}-\text{Si})^\circ$, in SiO_2 glass from fitting of ^{29}Si MAS NMR spectra to an angle distribution function. Note that the maximum corresponds to that of cristobalite at its liquidus temperature (1723 °C), and is also similar to that obtained from X-ray diffraction of SiO_2 glass. A recent ^{17}O NMR two-dimensional dynamic angle study resulted in 147° [3]. These angle distributions are consistent with a SiO_2 glass structure comprising predominantly six-membered rings of three-dimensionally interconnected SiO_4 tetrahedra.

charge-balancing or a network-modifying role [5]. The type and proportion of charge-balancing cations also are important because of their different effect on the energetics of the O–Al bonds and, therefore, on glass and melt properties. This is seen, for example, in enthalpy of solution (Figure 3), viscosity, and also in melt and glass density, compressibility, and thermal expansion.

The glass structure along SiO_2 – MAIO_2 joins (M = alkali metal as charge-balancing cation – meta-aluminosilicate; see Figure 1) is a continuous evolution of the SiO_2 glass structure with substitution of Al^{3+} for Si^{4+} in tetrahedral coordination and with only a very small percentage or fraction of a percent of Al^{3+} in different structural roles. There is marginally more Al^{3+} in such roles in glasses along the SiO_2 – CaAl_2O_4 join [7].

The K^+ , Na^+ , and Ca^{2+} are the dominant charge-balancers in natural magmatic liquids (Figure 4). For melts and glasses with multiple potential cations for Al^{3+} charge-balance, thermodynamic data can be used to establish relative stability of aluminate complexes. There is near equal stability of $(\text{KAl})^{4+}$ and $(\text{NaAl})^{4+}$ charge-balance followed by $(\text{Ca}_{0.5}\text{Al})^{4+}$. In natural rocks, the proportion of Ca^{2+} relative to $(\text{Na}^+ + \text{K}^+)$ decreases with increasing SiO_2 concentration so that in rhyolite melt, for example, alkalis dominate over Ca^{2+} for

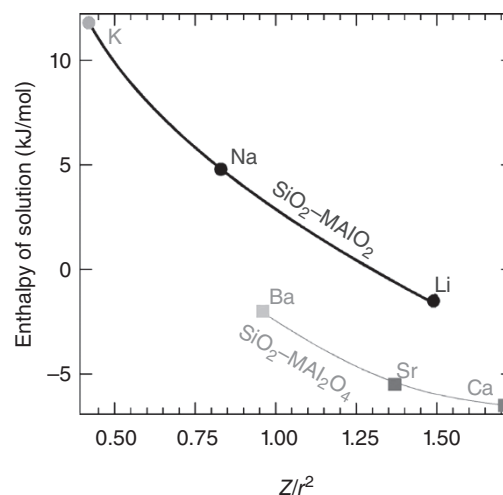


Figure 3 Energetics of Al,Si substitution along meta-aluminosilicate joins as a function of ionization potential, Z/r^2 , of metal cation that serves to charge-balance Al^{3+} in tetrahedral coordination (ionic radius, r , assumed that of six-coordinated metal cations – data from [6]). Heat of solution of glasses in molten lead borate solution is used as a measure of the substitution energetics. Simple and systematic relations with Z/r^2 are evident, but with distinct separation of relationships for cations with different charge-balancing cations. This difference stems from different substitution mechanisms of Al^{3+} for Si^{4+} depending on whether the charge-balance is accomplished with monovalent or divalent cations.

charge-balancing of Al^{3+} . For less silica-rich melts, the main charge-balancing cation is Ca^{2+} . For commercial glass such as glass wool, Na^+ is the principal charge-balancing cation for tetrahedral Al^{3+} , whereas in rock wool with a composition more akin to natural basalt (Table 1; see also [1], chapter 18), alkali metals and Ca^{2+} serve to charge-balance Al^{3+} together. Somewhat similar structural features can be found in the glass containment of incinerated household waste.

3 Metal Oxide–SiO₂ Systems

3.1 General Remarks

In order to characterize the structure of depolymerized, chemically complex aluminosilicate glasses and melts (Figure 1), it is first necessary to describe the structure of simple binary metal oxide–silica compositions. With this information, one can then consider multicomponent metal oxide silicate and aluminosilicate glasses and melts.

The metal oxides in multicomponent metal oxide–silica systems usually are K_2O , Na_2O , CaO , and MgO . In Al-free silicate glasses such as window and container glass, for example, these oxides serve only as

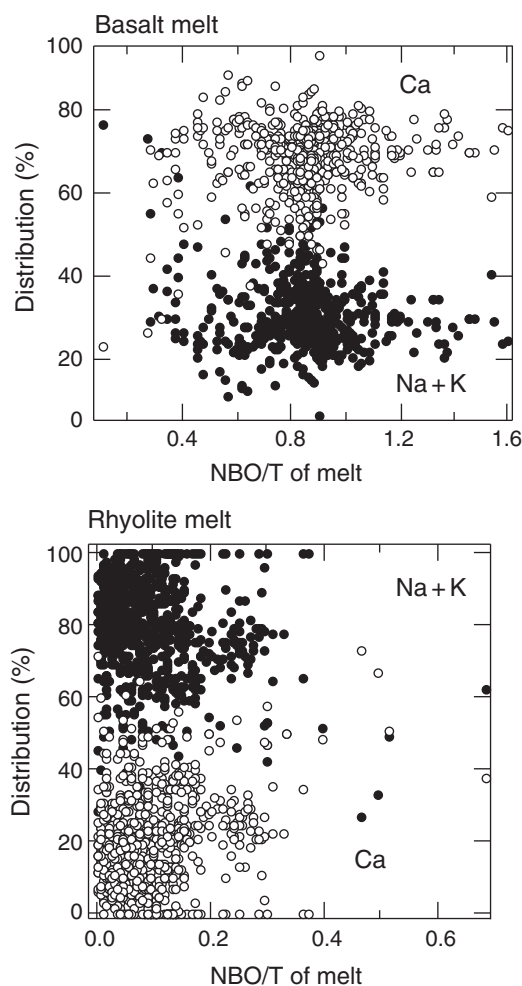


Figure 4 Summary of distribution of charge-balancing cations ($\text{Na}^+ + \text{K}^+$ and Ca^{2+}) in natural magmatic liquids of basalt and rhyolite melt compositions as a function of the NBO/T of the melts. The summary was developed from chemical data in <http://Earthchem.org>. This web site contains a compilation of analyses of rocks in the published literature, where the individual rock names are those given in the source of the database. As seen in Figure 5, for each of these types of rocks, the NBO/T of their melts comprises a wide range. See Table 1 for average compositions of basalt and rhyolite.

network-modifiers. Glass used in television and computer monitors and in optical fibers comprises additional network-modifying cations including rare earths, large alkaline earths (Sr^{2+} and Ba^{2+}) and, sometimes, transition metals. In natural magmatic liquids, these cations can serve both as network-modifiers and to charge-balance Al^{3+} in fourfold oxygen coordination as described in Section 2.2. Similar compositions and structural environments can be found in glass and rock wool, E glass, and Vycor.

The properties and behavior of SiO_2 in metal oxide silicate melts and glasses differ somewhat from those of pure silica glass and melt. The partial molar volume of this component is slightly smaller ($26.8 \text{ cm}^3/\text{mol}$) than

the volume of pure SiO_2 ($27.3 \text{ cm}^3/\text{mol}$) because some of the oxygen in these glasses and melts are nonbridging (NBO) and the partial molar volume of NBO is slightly less than that of bridging oxygen. In metal oxide silicate, the partial molar volume of SiO_2 is independent of composition, however, over wide composition range [8]. Systematic relations between metal/silicon ratio can also be seen in other physical and chemical properties such as viscosity, conductivity, thermal expansion, and compressibility of glasses and melts [1].

In ternary and more complex metal oxide silica melts, the values of most properties cannot be described as linear combinations of the endmembers (*mixed alkali effect*). For example, window glass, which is essentially a mixture of Ca- and Na-silicate components, is in this category. This behavior is related to the steric effects that govern metal cation ordering among different NBO in ternary and more complex metal oxide- SiO_2 glasses and melts. Ordering affects configurational and mixing properties and, therefore, rheological and thermodynamic properties. The greater the contrast in electronic properties such as their electrical charge and ionic radius of the network-modifying cations, the greater the effect of mixing on melt and glass properties. This ultimately leads to liquid immiscibility in SiO_2 -rich metal oxide- SiO_2 melts. In fact, at given temperature the width of the immiscibility gap is a positive function, Z/r^2 (Z = formal electrical charge, r = ionic radius), of the metal cation.

3.2 Structure

Structural characterization of simple and complex metal oxide silicate glasses and melts can be expressed in terms of nonbridging oxygen, NBO, per tetrahedrally coordinated cation, T (Chapter 2.4). The NBO/T-values of commercial glasses range from about 0.2–0.3 (for Pyrex glass, for example) to values greater than 3.0 for some slags (Chapter 7.4). The NBO/T of typical window glass is about 0.8, which is similar to those of rock wool. In nature, the NBO/T-values of melts from individual rock types fall within relatively broad ranges (Figure 5). In general, there is a negative correlation between the NBO/T-value and the SiO_2 concentration.

The distribution of network-modifying cations in complex systems is linked to both their alkali metal/alkaline earth ratio and the types of metal cations available for charge-balance of tetrahedrally coordinated Al^{3+} . For the most part, the network-modifying cations in natural magma are alkaline earths because their Na + K components charge-balance tetrahedrally coordinated Al^{3+} . Among the network-modifying cations, Mg^{2+} is exclusively a network-modifier, whereas Ca^{2+} is used both to charge-balance Al^{3+} and to serve as a network-modifier (Figure 6).

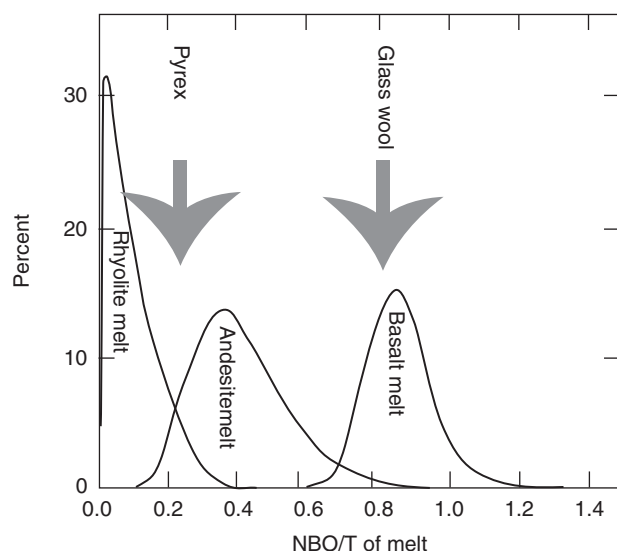


Figure 5 Calculated distribution of NBO/T-values of major groups of natural magma compositions derived from the database, <http://Earthchem.org>. Also shown (arrows) are approximate NBO/T-values for Pyrex glass and glass wool. Average basalt and rhyolite compositions are shown in Figure 4.

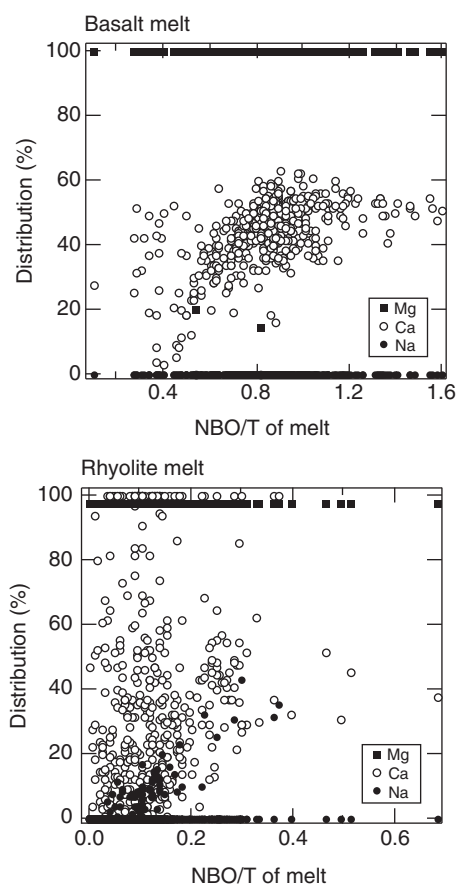


Figure 6 Distribution of network-modifying cations (Na⁺, Ca²⁺, and Mg²⁺) in natural magmatic liquids of basalt and rhyolite melt compositions as a function of the NBO/T of the melts. The summary was developed from chemical data in <http://Earthchem.org>.

3.3 Speciation, Cation Mixing, and Ordering

The NBOs in glasses and melts are not equivalent energetically. Instead, the structure of metal oxide–SiO₂ glass and its precursor melt is described in terms of a small number of distinct coexisting silicate structural units commonly described as Q^n -species with $n = 0, 1, 2, 3$, and 4 where n is the number of bridging oxygen (Chapter 2.4). The overall degree of polymerization, NBO/T, is related to Q^n -species abundance:

$$\frac{\text{NBO}}{\text{T}} = \sum_{n=0}^{n=4} (n-4)X_{Q^n}, \quad (1)$$

where X_{Q^n} is the mol fraction of the Q^n -species and n is the number of bridging oxygen in the individual Q^n -species. The NBO/T-parameter itself does not distinguish between different types of NBO.

The abundance of individual Q^n -species changes with metal oxide/SiO₂ ratio of the material (Figure 7). In simple binary metal oxide–silica melts, the abundance of Q^3 , Q^2 , and Q^1 species reaches maximum values at stoichiometries near NBO/Si = 1, 2, and 3, respectively, and decreases on both sides of these maxima. Orthosilicate compositions comprise both Q^1 and Q^0 species with free oxygen compensating for the presence of the polymerized Q^1 structure. The Q^n -species abundances also are affected by the ionization potential, Z/r^2 (Z : formal electrical charge, r : ionic radius), of the metal cation (Figure 7) because steric hindrance near the NBO governs how individual metal cations will distribute themselves among the Q^n -species. The ordering of alkalis and alkaline earths among energetically nonequivalent NBO in different Q^n -species in multicomponent compositions also aids in the explanation of the mixed alkali effect. For comparison, in crystalline metal oxide–SiO₂ systems, analogous steric hindrance effect instead limits the minimum metal oxide/SiO₂ ratio of the crystalline materials below which crystalline compounds are not stable [9].

In the much more chemically complex natural magmatic liquids, Q^n -species distributions resemble those observed for binary metal oxide glasses and melts [10]. The influence of individual network-modifying cations is difficult to establish, however, because of wide ranges of compensating effects on structure from the large number of different network-modifying cations.

Whether in simple binary metal oxide silicates or more complex systems, the equilibrium constant for the principal expression that describes the equilibria among the Q^n -species, $2Q^n \rightleftharpoons Q^{n-1} + Q^{n+1}$ (see Chapter 2.4), is positively correlated with Z/r^2 at least for systems for which $n = 3$ in the aforementioned reaction to yield $2Q^3 \rightleftharpoons Q^2 + Q^4$ (Figure 8). The enthalpy change of the latter reaction at temperatures above the glass transition is also a positive function of the Z/r^2 of the metal cation and is more sensitive to Z/r^2 of the more polymerized (lower bulk

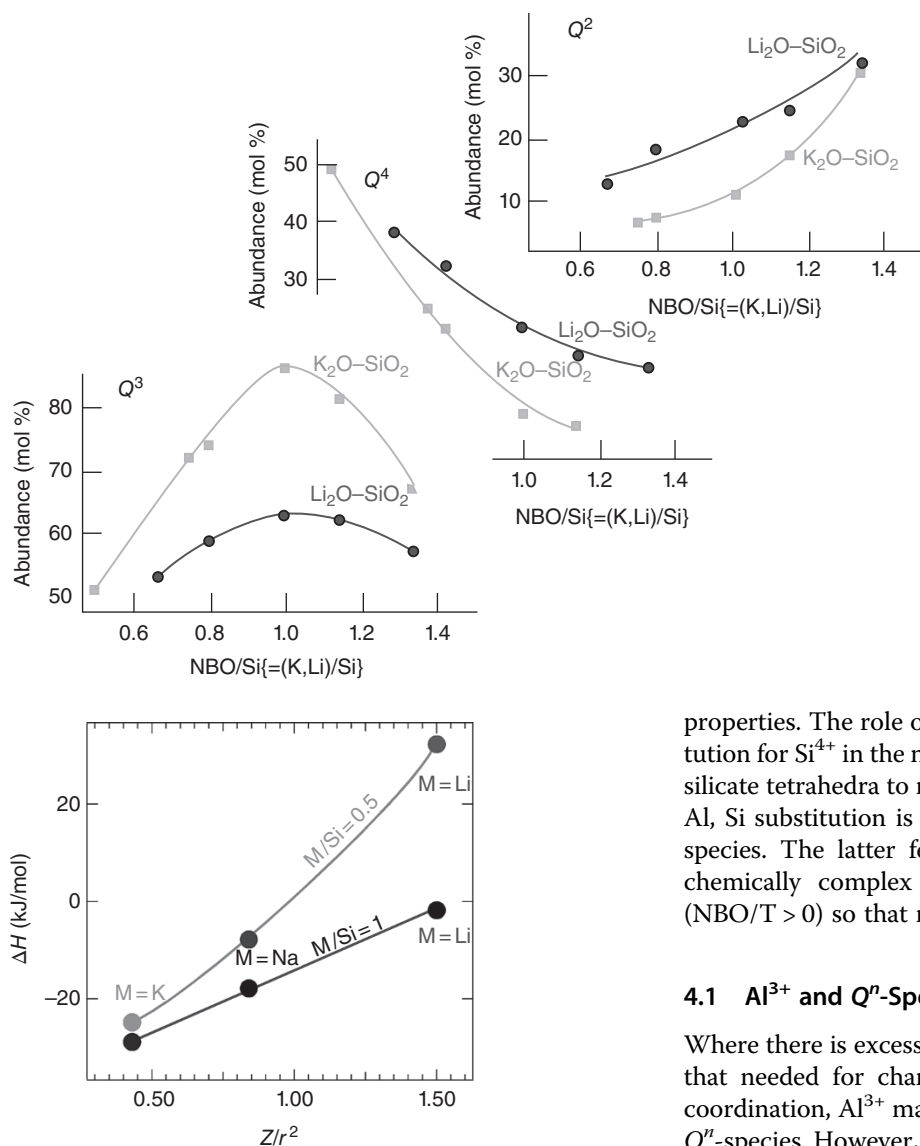


Figure 8 Enthalpy change, ΔH , for the disproportionation equilibrium, $2Q^n \rightleftharpoons Q^{n-1} + Q^{n+1}$, $n = 3$, as a function of ionization potential of alkali cation for two series of alkali metal (M) silicate compositions. In these systems, $M/Si = NBO/Si$ assuming all Si^{4+} is in tetrahedral coordination in the glasses. The ΔH is derived from temperature-dependent equilibrium constant at temperatures above the glass transition and assuming that mol fraction of Q^n -species equals their activity. Note that the ΔH -value increases with increasingly polymerized melts probably as a result of increasingly nonideal mixing of the Q^n -species. (Source: Modified after [8].)

NBO/Si-value) silicate melt (Figure 8). This relationship obtains because steric hindrance near NBOs diminishes with decreasing average values of n of the Q^n -species.

4 Aluminum and Aluminate

Characterization of the structural roles of Al^{3+} in aluminosilicate compositions is central to understanding their

Figure 7 Abundance evolution (mol %) of Q^2 , Q^3 , and Q^4 species in alkali silicate glasses as a function of their NBO/Si-values of compositions as indicated in diagrams. For alkali silicate glasses, the metal/silicon ratio equals the NBO/Si, provided that all Si^{4+} is in tetrahedral coordination. The ionization potential, Z/r^2 , of K^+ and Li^+ is 0.46 and 1.49, respectively, assuming sixfold coordination of oxygen around the alkali metal. The curves for Na_2O-SiO_2 (Z/r^2 of Na^+ : 0.8) fall in between those of Li_2O-SiO_2 and K_2O-SiO_2 .

properties. The role of Al^{3+} can vary from simple substitution for Si^{4+} in the network of interconnected aluminosilicate tetrahedra to more complex environments where Al, Si substitution is restricted to only some of the Q^n -species. The latter feature is important because most chemically complex compositions are depolymerized ($NBO/T > 0$) so that multiple Q^n -species will coexist.

4.1 Al^{3+} and Q^n -Species

Where there is excess alkali metal or alkaline earths over that needed for charge-balance of Al^{3+} in tetrahedral coordination, Al^{3+} may be distributed among the various Q^n -species. However, this distribution is not random and Al^{3+} dominantly is in Q^4 -species. Coexisting, less polymerized Q^n -species are essentially devoid of Al^{3+} . This situation reflects the tendency of Al^{3+} to substitute for Si^{4+} in SiO_4 tetrahedra with the smallest intertetrahedral angle, which is found in Q^4 -species.

It follows that the equilibrium constant for the reaction, $2Q^3 \rightleftharpoons Q^2 + Q^4$, is positively correlated with $Al/(Al + Si)$ of the glass and melt. For peralkaline alkali aluminosilicate melts (see Figure 1) at temperatures above their glass transition, the temperature-dependent equilibrium constant yields ΔH -values increasing from near 0 to about 40 kJ/mol in the $Al/(Al + Si) = 0-0.4$ range. Fewer experimental data exist for peralkaline alkaline earth aluminosilicate glasses.

In chemically complex environments with both alkalis and alkaline earths present, the alkali metals associate with the Al^{3+} in the Q^4 species, whereas alkaline earths tend to bond with NBO in depolymerized species [10]. It follows, therefore, that for systems such as natural magmatic

liquids, the Q^n -distribution is controlled for the most part by the rules that govern alkaline earth compositions.

This can be illustrated with the use of experimental data from ternary aluminosilicates to model the properties of chemically more complex systems. For example, the physicochemical properties of aluminosilicate glasses and melts, which vary with (Si,Al)—O bond energy, can be related qualitatively, and sometimes semi-quantitatively, to the Al/(Al + Si) ratio and to the electronic properties of charge-balancing cation because the bond energy varies with these same variables. The viscosity and activation energy of viscous flow of melts along meta-aluminosilicate joins, which are essentially fully polymerized, follow such simple evolutions within temperature intervals where the temperature-dependent viscosity is approximately Arrhenian (Figure 9). In contrast, the viscosity of peralkaline aluminosilicate melts does not show this effect of Al/(Al + Si) and actually may have a minimum at intermediate Al/(Al + Si)-values (Figure 9). This difference is because of a combination of weakening of (Si,Al)—O bonds in Q^4 -species with increasing Al/(Al + Si) and changing Q^n -species abundance with increasing Al/(Al + Si).

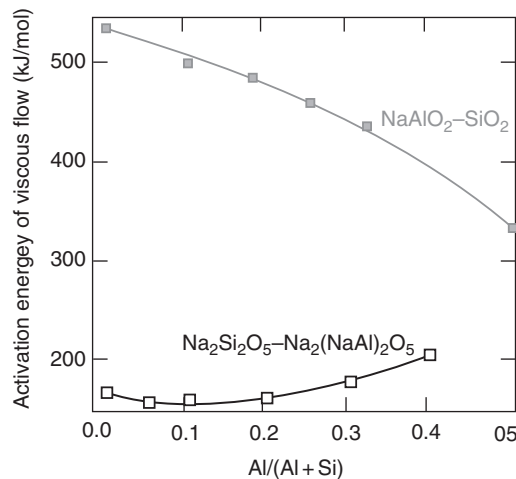


Figure 9 Activation energy of viscous flow of aluminosilicate melts along the NaAlO₂—SiO₂ (nominal NBO/T = 0) (meta-aluminosilicate) join (closed squares) and Na₂Si₂O₅—Na₂(NaAl)₂O₅ (nominal NBO/T = 0.5) (peralkaline aluminosilicate) calculated with the assumption of Arrhenian viscosity of the melts. As discussed in the text, NaAlO₂—SiO₂ melts and glasses do have a small fraction of a percent nonbridging oxygen, but are essentially pure Q^4 with Al-substitution for Si. Melts and glasses on the Na₂Si₂O₅—Na₂(NaAl)₂O₅ join, on the other hand, comprise Q^2 , Q^3 , and Q^4 species with essentially all Al³⁺ in substitution for Si⁴⁺ in the Q^4 species thus weakening the (Si,Al)—O bridging oxygen bonds in this specie. This, in turn, lowers the activation energy as for the NaAlO₂—SiO₂ melts and glasses. However, because of Al-preference, the proportions of Q^n -species change so that Q^4 abundance increases, thus countering the effect of the Al,Si-substitution. These two mechanisms give rise to the minimum activation energy values at intermediate Al/(Al + Si) values.

The compressibility and thermal expansion of alkali aluminosilicate melts are also correlated with Al/(Al + Si) because the intertetrahedral (Si,Al)—O—(Si,Al) angle is itself more compressible and expandable with increasing Al/(Al + Si). In alkaline earth aluminosilicate systems, however, the opposite relations exist because Ca-charge-balanced Al³⁺ causes the (Si,Al)—O—(Si,Al) bonds to stiffen. In other words, the compressibility and thermal expansion of such aluminosilicate melts decreases with increasing Al/(Al + Si).

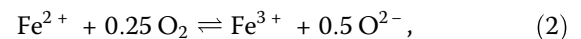
Among the main groups of natural magmatic liquids (basalt, andesite, and rhyolite), the proportion of alkaline earths/alkali metals in charge-balancing roles decreases in the same order. This means that basaltic melts are less compressible and show smaller thermal expansion than more silica-rich melts such as rhyolite. Furthermore, the viscosity of basalt melt is less sensitive to Al/(Al + Si) than more silica-rich magma, which have a higher proportion of alkali-charge-balanced Al³⁺ in tetrahedral coordination.

5 Ferric and Ferrous Iron

Iron is found in three redox states, Fe⁰, Fe²⁺, and Fe³⁺, but only the last two can enter the structure of silicate compositions in significant amounts. In this environment, the proportions of Fe²⁺ and Fe³⁺ vary with bulk chemical composition of glasses and melts, temperature, pressure, and redox conditions during equilibration of precursor melt. In magmatic liquids, the Fe³⁺/ΣFe ranges from essentially 0 to 1 (Figure 10) in such a way that this redox ratio has been employed to estimate the activity of oxygen and, therefore, oxygen budgets during formation and evolution of earth materials and, indeed, the Earth, itself.

5.1 Redox Relations of Iron

Equilibria between Fe³⁺ and Fe²⁺ in silicate melt and glass include interaction with oxygen in the structure. Conversely, variations in redox behavior of iron oxides affect the silicate melt structure. From the simple relationship,



where O²⁻ is the link to the silicate structure, the relationship between redox ratio and oxygen fugacity provides a measure of the activity coefficient ratio of Fe³⁺ and Fe²⁺, $g_{\text{Fe}^{3+}}/g_{\text{Fe}^{2+}}$. This ratio often is about 1, but does depend on silicate polymerization (Figure 11). The redox ratio also varies with Al/(Al + Si) and the electronic properties of the metal cations. It increases with Al/(Al + Si) and NBO/T. The redox ratio also increases the more electro-positive the network-modifying cation. This means, for example, that the Fe³⁺/Fe²⁺ of alkali silicate melts is

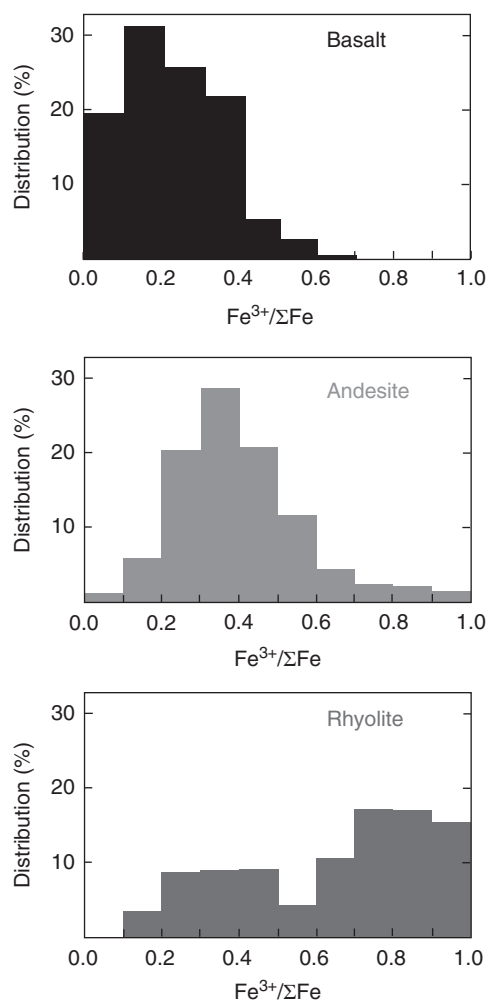


Figure 10 Distribution of redox ratio of iron ($\text{Fe}^{3+}/\Sigma\text{Fe}$) among various common rock types. Database: <http://Georock.org>. Examples of average compositions of basalt, andesite, and rhyolite are given in Figures 5 and 6.

greater than that of alkaline earth silicate melts at the same temperature (pressure) and redox conditions.

5.2 Structural Roles of Fe^{3+} and Fe^{2+}

It is sometimes assumed that Al^{3+} and Fe^{3+} occupy similar structural positions in silicate melts and glasses because of their common nominal charge and somewhat similar ionic radii. But this assumption is not necessarily warranted because Al^{3+} is dominantly in fourfold coordination in silicate crystals, whereas for the most part Fe^{3+} is in sixfold coordination with oxygen although there are exceptions to this general statement.

In silicate glasses and melts oxygen coordination numbers vary with bulk chemical composition, total iron content, temperature, and redox conditions that existed

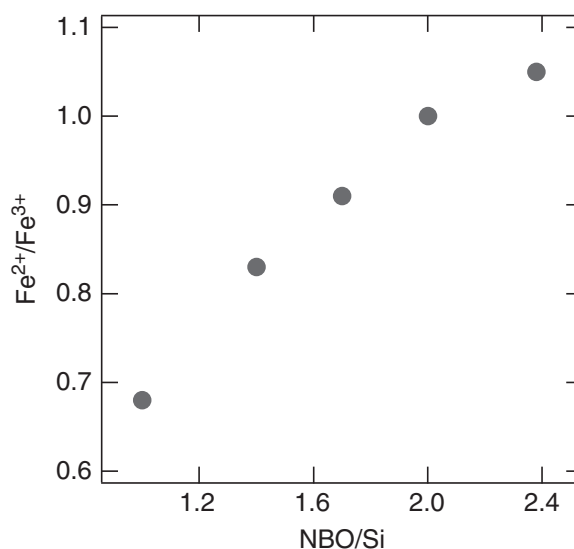


Figure 11 Activity coefficient ratio of Fe^{2+} and Fe^{3+} in CaO-SiO_2 glasses formed by quenching from melt after equilibration at 1600°C with different oxygen fugacity. The NBO/Si -values in this figure were calculated from the Ca/Si ratio. From the relationship to oxygen fugacity, any deviation of the concentration ratio, $\text{Fe}^{2+}/\text{Fe}^{3+}$, was ascribed to changes in the activity coefficient ratio, $g_{\text{Fe}^{2+}}/g_{\text{Fe}^{3+}}$, because $(g_{\text{Fe}^{2+}}/g_{\text{Fe}^{3+}})(\text{Fe}^{2+}/\text{Fe}^{3+}) = 0.25$.

during precursor melting. The $\text{Fe}^{3+}\text{-O}$ bond distance of ferrisilicate glass is often used as an indicator of oxygen coordination number. For example, increasing iron content in Al -free silicates results in increasing $\text{Fe}^{3+}\text{-O}$ distance, which may be consistent with a transformation from fourfold to sixfold coordination.

Mössbauer spectroscopy of glasses is an analytical tool with which both redox ratio of iron and coordination of Fe^{3+} and Fe^{2+} can be determined (Chapter 2.2). In alkali ferrisilicate melts equilibrated with air, Fe^{3+} typically is in fourfold coordination with oxygen. However, by replacing Na^+ with more electronegative metals, the oxygen tetrahedra surrounding Fe^{3+} become increasingly distorted with an eventual changes to higher oxygen coordination numbers. As a result, in complex aluminosilicate compositions containing both alkalis and alkaline earths it is not unusual that Fe^{3+} exists in more than one coordination state.

Most evidence suggests that Fe^{3+} in fourfold coordination forms oxygen tetrahedra that are isolated from those of Si^{4+} and Al^{3+} . Furthermore, when both alkali and alkaline earths are potential charge-balancing cations in complex systems, alkali metals tend to associate with Al^{3+} , whereas alkaline earths serve to charge-balance Fe^{3+} in tetrahedral coordination with oxygen. This means, for example, that if a rhyolite and a basalt melt equilibrated at the same oxygen fugacity, temperature, and pressure, the iron would be more oxidized in the rhyolite than in the basalt melt.

At least in FeO—SiO₂ systems the Fe²⁺—O distances are consistent with sixfold coordination although it has also been suggested that the oxygen coordination number of Fe²⁺ might be closer to 4 than to 6. Results from ⁵⁷Fe Mössbauer resonant absorption spectroscopy of iron-bearing glasses offer additional aid to distinguish between possible oxygen coordination numbers of ferrous iron (4, 5, and 6).

5.3 Structure–Property Relations

The physical properties of iron-bearing silicate melts and glasses are less well known than for iron-free materials. Viscosity and volume data can nonetheless be rationalized in structural terms.

The partial molar volumes of FeO and Fe₂O₃, $\bar{V}_{\text{FeO}}$ and $\bar{V}_{\text{FeO}_{1.5}}$, are sensitive to oxygen coordination. The $\bar{V}_{\text{FeO}}$ in glass (between about 13 and 14 cm³/mol) resembles the molar volume of crystalline wüstite (FeO), which suggests that Fe²⁺ is sixfold coordinated in glasses. The $\bar{V}_{\text{FeO}_{1.5}}$ -values are more variable, however, and depend on composition. For example, in SiO₂—NaFeO₂ glasses formed by quenching from melt equilibrated with air (and with Fe³⁺/SFe > 0.95), $\bar{V}_{\text{FeO}_{1.5}}$ is between 20 and 21 cm³/mol (as FeO_{1.5}), whereas for equivalent Ca-ferrisilicate melt, $\bar{V}_{\text{FeO}_{1.5}} = 13\text{--}15$ cm³/mol [11]. These latter volumes are those expected with Fe³⁺ in tetrahedral and octahedral coordination, respectively.

The viscosity of iron-bearing silicates depends on both redox state of iron and on the coordination state of Fe²⁺ and Fe³⁺. For example, with Fe³⁺ in fourfold coordination and Fe²⁺ in sixfold coordination with oxygen, melt viscosity increases systematically with increasing Fe³⁺/SFe because silicate polymerization also increases with increasing Fe³⁺/SFe [12]. When both Fe³⁺ and Fe²⁺ are surrounded by octahedral oxygen ligands, this relationship is reversed. Given that the redox ratio in basaltic melts normally is considerably lower and the oxygen coordination number around Fe³⁺ higher than in more silicate rich melts (andesite and rhyolite, for example), decreasing Fe³⁺/Fe²⁺ in the former may result in increased melt viscosity, whereas the opposite trend obtains for the latter.

6 Minor Components in Silicate Glasses and Melts

Minor components such as TiO₂ and P₂O₅ are important in natural and commercial glasses, including optical fibers and glass wool insulating materials. The structural behavior of P⁵⁺ in silicate glasses and melts is fairly well known, whereas that of Ti⁴⁺ remains more controversial, perhaps

because the oxygen coordination environment surrounding Ti⁴⁺ may be a composition-dependent variable.

6.1 Phosphorus Substitution for Silicon

In P₂O₅ glass, the P—O bridging bond distance (1.60 Å) is nearly identical to the Si—O distance in SiO₂ glass (1.62 Å). Additionally, there is a second double-bonded and shorter (1.43 Å) P=O bond. These structural features remain for glasses in the P₂O₅—SiO₂ system. In the latter, Si—O—P bridges can also be detected.

Phosphorus in metal oxide silicate and aluminosilicate glasses and melts is dissolved by formation of phosphate (PO₄) groups. Their degree of polymerization can be derived from ³¹P NMR spectra as a function of metal oxide/P₂O₅ ratio [13] in a way similar to Qⁿ-species determinations in metal oxide—SiO₂ glasses (see also Chapter 2.4 and Section 3.1). In addition, there are minor contributions from Si—O—P linkages. Mixed alumino-silico phosphate complexes are more common (Chapter 2.4).

6.2 Multiple Roles of Ti⁴⁺

The ionic radius of Ti⁴⁺ is nearly twice that of Si⁴⁺. It is not surprising, therefore, that Ti⁴⁺ in crystalline materials commonly occupies sixfold coordination, whereas Si⁴⁺ is in tetrahedral coordination. In glasses and melts, on the other hand, the structural behavior of Ti⁴⁺ is more complex. From partial molar volume of TiO₂, $\bar{V}_{\text{TiO}_2}$ -values near 30 cm³/mol in alkali silicate and $\bar{V}_{\text{TiO}_2}$ to be ≤25 cm³/mol in alkaline earth silicate point to different structural behavior governed by the nature of the metal cations [8].

Raman and XANES spectroscopic data of SiO₂—TiO₂ glasses suggest Ti⁴⁺ in five- and sixfold coordination with oxygen at low concentrations (<3 mol % TiO₂), whereas in more concentrated solution, Ti⁴⁺ is surrounded by four oxygens. However, it also has been suggested from X-ray and neutron diffraction data that fourfold coordination dominates at low TiO₂ concentrations in alkali silicate glasses, whereas fivefold coordination is more important at higher concentrations. The latter conclusions are in qualitative agreement with inferences drawn from Raman spectra of alkali aluminosilicate glasses. In aluminosilicate glasses, the Al/(Al + Si) ratio also affects the oxygen coordination number around Ti⁴⁺.

7 Perspectives

We are poised to advance our understanding of silicate compositions from empirical modeling, based on current understanding of property–structure relationships and

simple oxide-based descriptions, to direct determination of the structure of complex systems. The anionic structural backbone is established. As indicated by the first steps taken in this direction, quantitative understanding of structural variations with composition and intrinsic variables is possible. Moreover, with increased miniaturization and micro-processing, measurements of glass and melt properties with samples under the conditions of interest are now feasible. It will also be possible to track and characterize structurally the kinetics of transformations, to quantify glass-forming processes, and, likely, to engineer properties of glasses on the basis of our rapidly advancing enhanced understanding of structure–property relations.

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2.7

Topological Constraint Theory of Inorganic Glasses

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1 Introduction

Compositional innovation has been the bedrock of glass R&D for more than a century. Two questions always come up when searching for a new composition: Will the material be easy to form into glass from the liquid and will its properties have the values desired for the application considered? This set of properties includes not only those of the finished glass product (mechanical, for example) but also those necessary for successful processing (such as melt viscosity and glass transition temperature, T_g). In principle, the topological constraint theory (TCT) can aid in providing answers to both of these questions.

Historically, TCT grew along two distinct paths, both starting at about the same time in the late 1970s. The more widely known view, termed the *bond constraint theory* (BCT), was formulated in 1979 by Phillips [1] and is most useful for *chemically disordered* covalent systems such as chalcogenides. The other view applies to *chemically ordered* systems such as oxide glasses whose structure, *à la* Zachariasen ([2], Chapters 2.1 and 3.1), consists of topologically disordered extended networks of corner-sharing rigid polyhedra. This view was developed by Cooper [3] in 1978 for two-dimensional networks and later extended to three-dimensional networks by Gupta and Cooper [4]. We refer to this view as the *polyhedral constraint theory* (PCT).

During the early development, constraints were counted as either intact (=1) or broken (= 0) and temperature (T) played no role. In 1993 [5] (and in more detail in 1999 [6]), Gupta introduced the concept of temperature-dependence of bond constraints. In 2009, Gupta and

Mauro applied the T -dependent BCT to rationalize the composition (x) dependence of the glass transition temperature $T_g(x)$ in binary chalcogenide [7] and in binary oxide systems [8]. Later, Bauchy and Micoulaut [9] validated the phenomenology of T -dependent bond constraints with molecular dynamics (MD) simulations.

With growing interest in TCT, much effort has been and is being invested in applying it to model the composition dependence of a variety of properties in glassy systems. The most successful thus far has been the work of Mauro and colleagues [10] for the composition dependence of the room-temperature hardness of oxide glass systems. Not being a comprehensive review, however, the present chapter does not include these recent applications. It is organized as follows: an introduction to TCT is presented in the Section 2. It establishes key definitions and terminology and outlines the underlying conceptual framework. In Section 3, elements of PCT and some of its applications to oxide glass-forming systems are presented. Section 4 does the same for BCT with examples from chalcogenide systems. In Section 5, we discuss the phenomenology of the temperature dependence of constraints – a development that has generated much excitement owing to its remarkable ability to model variations of properties with composition. Some fundamental issues associated with TCT are discussed in Section 6 along with suggestions for possible ways to embed the TCT phenomenology within the general framework of the potential energy landscape (PEL) of liquids and glasses.

Not many comprehensive reviews of TCT are available in the literature. Early on, Phillips [11] published an introductory paper on BCT entitled “The Physics of Glass.” Thorpe [12] provided an account of the early developments of the rigidity percolation theory. Gupta [5] reviewed the PCT formalism in 1993 and later more extensively in 1999 [6]. Recently, Naumis and

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Romero-Arias [13] have reviewed the physics of the constraint theory, its connection with thermodynamics and with glass transition. More recently, Mauro [14] has published an excellent introduction on TCT.

List of Acronyms

TCT	topological constraint theory
BCT	bond constraint theory
PCT	polyhedral constraint theory
PEL	potential energy landscape
TD	topologically disordered

2 Concepts of the Topological Constraint Theory

Network-based concepts enter naturally in TCT, which treats a glass-forming system as an atomic network where atoms constitute the nodes (or vertices) and atomic interactions (i.e. chemical bonds) constitute the edges (or linkages) of the network. The properties of an atomic network depend both on its chemistry (how atoms of different species are placed on its nodes) and on its topology (how various nodes are interconnected without regard for the nature of atoms).

2.1 Network Chemistry

2.1.1 Composition of an Atomic Network

When a network contains only one kind of atom (i.e. the network is chemically homogeneous), it is called one component (or unary). Networks are termed binary when they contain only two kinds of atoms, and multicomponent if three or more distinct atoms are present. The (molar) fractions $\{x_i\}$ of atoms of the different components specify the average chemical composition of a network. In this paper, we discuss only unary or binary networks of type $A_xB_{(1-x)}$, where x represents the mole fraction of A atoms.

2.1.2 Chemical Order and Disorder

For a given x , the arrangement of A and B atoms on the vertices of a network determines the nature of the chemical order present. Often, for networks having compound-like compositions, $A_C B_V$ (where C and V are integers), the arrangement of two types of atoms is well defined: every A atom is coordinated by a number, V , of B atoms. Similarly each B atom is coordinated by another number, C , of A atoms. Such networks with well-defined chemical arrangement are called *chemically ordered*. In these networks, linear bonds exist only

between dissimilar atoms (i.e. heteropolar bonds). A prime example of such networks is that of silica (SiO_2): each silicon is coordinated by four oxygens ($V = 4$) and each O is linked to two silicons ($C = 2$).

Not all glasses can be chemically ordered as this state can be achieved only for some definite stoichiometries. Noncompound-like compositions are thus necessarily disordered. A signature of chemical disorder is the presence of homopolar bonds (between similar atoms). Even compound-like compositions can be chemically disordered in covalent systems because of the presence of a significant fraction of such homopolar bonds: an example is GeSe_2 [15].

2.1.3 Atomic Interactions and Chemical Bonds

Bonds constituting the edges of an atomic network represent simple mappings of atomic interaction potentials among the constituent atoms. For the purpose of TCT:

- Pair interactions are mapped into narrow potential wells, forming *linear bonds* of fixed length between neighbors. The tails of pair interaction potentials are ignored. Whereas this assumption is reasonable for short-range interactions, its validity is questionable for long-range coulombic potential, especially in BCT.
- Among many-body interactions, only triplet interactions are retained. They, together with next-nearest neighbor pair interactions, form the *angular bonds* at the vertices. Whereas angular constraints are important in BCT, they do not play any direct role in the PCT.

2.1.4 Structural Units in Chemically Ordered Networks

In a binary chemically ordered network, each A atom is coordinated by exactly the same number (V) of B atoms. Hence, the network can be viewed as made up of well-defined polyhedral (AB_V) structural units having an A atom in the center and a B atom at each vertex (i.e. corner). Further, C such structural units are connected in the network to each B atom. The chemical formula of the structural unit, $AB_{(V/C)}$, is therefore the same as that of the network as a whole.

2.2 Network Topology

For topological considerations, an atomic network is treated as if the observer is “chemically blind.” In other words, the network is considered simply as a combination of vertices and edges disregarding the nature of the atoms occupying the vertices. Thus, topology refers only to how the nodes are interconnected in a network.

Local (or short-range) topology at the i th vertex is described by the number (r_i) of edges shared by that

vertex (i.e. the vertex coordination number). A vertex having $r_i = 1$ is called non-bridging or dangling. Vertices with $r_i > 1$ are called bridging (or network-forming). When r_i is the same for all vertices, the network is called regular. Otherwise, it is irregular. For an irregular network, the average vertex coordination number, r , also called the *connectivity*, provides a measure of its short-range topology. Note that, in chemically ordered networks, r is related to the two coordination numbers V and C by

$$r = \frac{2CV}{(C + V)}. \quad (1)$$

The intermediate-range topology of a network is characterized by its ring-size distribution so that it, for instance, depends on whether neighboring structural units share edges or corners. By definition, noncrystalline networks have no long-range topological order. For this reason, they are termed *topologically disordered* (TD) networks [4].

2.3 Bond Constraints

The edges of a network represented by linear bonds constitute linear constraints on the coordinates of the vertices. In atomic networks, angular bonds give rise to additional constraints at the vertices. The linear and angular constraints, together, are called bond constraints. Since an angular constraint can be viewed simply as the result of an additional cross-linear bond between next-nearest neighbors, the linear and angular constraints carry equal weights. In other words, during constraint counting, one angular constraint and one linear constraint add up to two constraints.

It is important to distinguish between independent and dependent (or redundant) constraints. Constraints in a network that do not change its deformation behavior are called dependent. Consider, for example, a finite planar network of four nodes situated at the corners of a square (Figure 1) for which the sides constitute four linear constraints. If these are the only constraints present, the network is *floppy* (i.e. it can be deformed). When a diagonal constraint is added, however, the network becomes *rigid*. When a second diagonal is added as the sixth constraint, no further change occurs in the deformation behavior of the network – it remains rigid. The sixth constraint, in this example, is therefore a dependent constraint. In TCT, it is important to count only the independent constraints and to exclude the dependent. To determine whether a constraint is dependent or not can be a challenging task. Owing to the presence of long-range topological order, crystalline networks contain a significant number of dependent constraints.

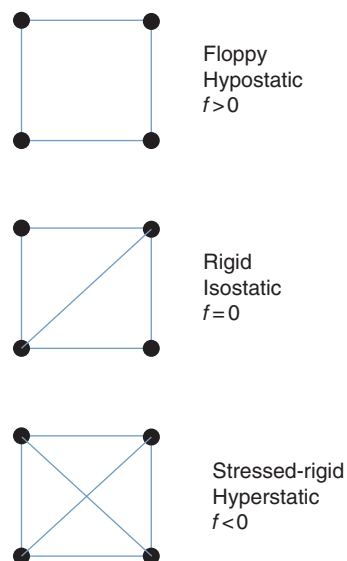


Figure 1 Deformation of a finite network of four nodes. Lines represent linear constraints. Top: floppy network (hypostatic, $f > 0$) with only four constraints originating from the edges. Middle: addition of a diagonal constraint makes the network rigid (isostatic with $f = 0$). Bottom: addition of a second, dependent diagonal constraint does not change the rigidity of the network.

Whereas one has to be extremely careful in applying constraint theory to crystals, this is fortunately not the case in noncrystalline TD networks.

2.4 Degrees of Freedom and the Network Deformation Modes

Without constraints (as, for example, in an ideal gas), each atom has d coordinate degrees of freedom where d is the dimension of the network. As constraints are added at a vertex, its coordinate degrees of freedom decrease. If n is the average number of independent constraints per vertex, then the average degrees of freedom per vertex, f , in a network is given by

$$f = d - n. \quad (2)$$

If $n < d$, then f is positive and the network can deform without expenditure of energy. Such a network is termed “floppy” (or hypostatic) and has exactly f floppy (soft or low frequency) modes per vertex. The number of degrees of freedom decreases as n increases. When $n > d$, the network is over-constrained and is termed “stressed-rigid” (or hyperstatic). The excess $(n - d)$ constraints in a stressed-rigid network are dependent if such a network exists. The transition from floppy to stressed-rigid takes place at $n = d$ (i.e. at $f = 0$), which marks the disappearance of floppy modes and the onset of network rigidity. Such a network is called *isostatic* (Figure 1).

In a floppy network, there may exist finite-size rigid inclusions (small group of atoms interconnected in a rigid manner) that are embedded in a floppy matrix. The average size of such rigid clusters grows as n increases till the rigid clusters begin to percolate, causing a transition from a floppy into a rigid network at $n = d$. Similarly, when a network is stressed-rigid ($n > d$), it may contain floppy clusters in a rigid matrix. The average size of these floppy clusters grows as n is reduced so that at $n = d$, the floppy clusters begin to percolate making the entire network floppy. Thus, a network undergoes a rigidity percolation transition at $f = 0$. This basic idea is at the heart of most TCT applications because n can vary with changes in both temperature and composition. In other words, since $n = n(T, x)$, the isostatic boundary in a T - x phase diagram is described by $n(T, x) = d$.

3 Polyhedral Constraint Theory

As mentioned before, PCT considers only chemically ordered networks which, according to Zachariasen [2], are TD networks of structural units made up of corner-sharing rigid polyhedra. In such networks, it is convenient to treat the shared corners of the polyhedra as the vertices and the polyhedral structural units as links. The rigidity of a network then arises from the rigidity of the structural units as well as from the vertex-connectivity condition (i.e. the fact that all corners of polyhedral units are shared among a certain number of units). These constraints resulting from the rigidity of structural units and connectivity are termed *polyhedral constraints*.

The deformation of a TD network is determined by the type of polyhedral structural units and by the vertex-connectivity (C) that specifies the number of polyhedral units sharing a vertex. The vertex-connectivity is related to (see Eq. 1) but is different from the average coordination number r .

3.1 Rigidity of Polyhedral Structural Units

An isolated single regular polyhedral unit can be specified by two parameters: the dimension (δ) of the unit and its number of vertices (V). The dimension of the unit is the minimum dimension necessary to embed it. For example, $\delta = 1$ for a rod, 2 for a triangular unit, and 3 for a tetrahedron. It is clear that $\delta \leq d$ (the dimension of the network) and that $V \geq (\delta + 1)$.

When a regular polyhedral structural unit is rigid, the total number, N_u , of independent constraints in the unit satisfies the following relation:

$$N_u = \delta V - \left[\frac{\delta(\delta + 1)}{2} \right]. \quad (3)$$

Table 1 Degrees of freedom (f) of d -dimensional TD networks of rigid units (δ, V) with C units sharing a vertex (with the assumption $h = \theta = 0$) based on Eqs. (4) and (5).

Structural unit	δ	V	n_u	d	C	f
Rod	1	2	0.5	2	3	0.5
				3	4	1
				3	6	0
Triangle	2	3	1	2	2	0
				3	2	1
Square	2	4	1.25	2	2	-0.5
Tetrahedron	3	4	1.5	3	2	0
				3	3	-1.5
Octahedron	3	6	2	3	2	-1
Cube	3	8	2.25	3	2	-1.5

Therefore, the number of independent constraints per vertex ($n_u = N_u/V$) in a rigid unit is

$$n_u = \delta - \left[\frac{\delta(\delta + 1)}{2V} \right]. \quad (4)$$

A major advantage of PCT is that Eq. (3) counts correctly the number of independent constraints in a rigid unit. From Eq. (4) and the values of n_u listed in Table 1 for several simple polyhedral units, one sees that n_u increases with both V (for fixed δ) and δ (for fixed $V > \delta$). When a structural unit is non-regular and rigid, other parameters, in addition to δ and V , are needed to specify the structural unit.

3.2 Existence of Topologically Disordered ($d = 3$) Networks

For an extended three-dimensional network (made up of a single type of structural unit) with an average C structural units sharing a vertex, the degrees of freedom, f , per vertex are

$$f = 3 - C \quad n_u = 3 - C \left[\delta - \left\{ \frac{\delta(\delta + 1)}{2V} \right\} \right]. \quad (5)$$

If f is positive, a network can exist. When f is negative, a TD network cannot exist. Thus, $f = 0$ provides a boundary for the existence of TD networks.

If additional constraints (θ) are present at the shared corners (for example, bond angle constraints) or if there are internal degrees of freedom (h) within the structural units (for example, there is one internal degree of freedom in a unit made up of a pair of edge shared tetrahedra), then Eq. (5) can be modified as follows:

$$f = (3 - \theta) - C \left[\delta - \left\{ \frac{\delta(\delta + 1)}{2V} \right\} - \left(\frac{h}{V} \right) \right]. \quad (6)$$

The degrees of freedom of TD networks are also listed in Table 1 for several rigid structural units for different values of connectivity. It should be noted that SiO_2 with $V = 4$, $C = 2$, $\delta = d = 3$ satisfies the condition of isostaticity ($f = 0$). Similarly, a two-dimensional TD network of corner-sharing rigid triangles (a candidate structure of B_2O_3 glass) is also isostatic.

3.3 Glass-forming Ability

According to PCT, a glass can be formed if and only if it can exist as a TD network (i.e. only if $f \geq 0$). With increasingly positive values of f , however, the existing TD network becomes progressively more floppy and may crystallize beyond a certain value $f(q)$ that depends on the cooling rate, q . Thus, glass formation is possible in the range for which $0 \leq f \leq f(q)$. With positive and increasing f , the potential energy of interaction (the chemical energy) increases because of unsatisfied chemical bonds. With decreasing and negative f , the strain energy in the system increases. In other words, an isostatic network represents a minimum in the total energy of the system. For this reason, the glass-forming ability is best under isostatic condition ($f = 0$) and becomes poor as f increases. The $f = 0$ boundary is termed the *isostatic boundary* of glass formation and the $f(q)$ boundary the *kinetic boundary* of glass formation.

3.3.1 Glass-forming Ability and the Condition of Isostaticity ($f = 0$)

The isostaticity condition is satisfied in three dimensions for tetrahedral structural units ($V = 4$) with two units sharing every vertex ($C = 2$) as is the case for SiO_2 , GeO_2 , and BeF_2 , which are known as excellent glass formers. The isostatic condition is also satisfied for two-dimensional networks made of corner-sharing triangles. This is often considered to be the reason why B_2O_3 is a strong glass former.

An interesting application of the isostatic boundary concept is identification of limiting isostatic composition for glass formation. Consider the example of nitridation of alkali-silicate glasses. In silicon oxynitride glasses, nitrogen substitutes for oxygen forming two kinds of vertices: oxygen vertices with $C = 2$ and nitrogen vertices with $C = 3$. Adding nitrogen to silica (for which f is 0) makes f negative. This suggests that nitridation of silica will be difficult. However, addition of alkali creates non-bridging oxygens (with $C = 1$). Thus, nitrogen can be added to alkali-silicates while keeping f non-negative. In fact one can calculate the maximum amount of nitrogen that can be incorporated into an alkali-silicate glass as

a function of the alkali content. Consider glass formation in an alkali silicon oxynitride system of the general composition $x \text{Na}_2\text{O} \cdot (1 - x)[\text{SiO}_{(2-y)} \text{N}_{(2y/3)}]$. Note that $0 \leq y \leq 2$ and $0 \leq x \leq 1$. This system has three types of vertices: non-bridging oxygens with $C = 1$, bridging oxygens with $C = 2$, and bridging nitrogens with $C = 3$. The isostatic condition gives the limiting solubility of nitrogen, $y_{\max} = 3x/(1 - x)$. For $y > y_{\max}$, f becomes negative. Whereas systematic investigations of nitridation of alkali-silicate glasses are not available, it is known that nitridation becomes easier upon increasing the alkali content [16].

Another example is provided by binary alkali-tellurite systems. Pure TeO_2 with trigonal bipyramid structural units is over-constrained and does not form glass. Glass formation improves upon addition of alkali oxide because of formation of non-bridging oxygens, thereby increasing f and thus making it possible to form glasses when sufficient alkali oxide is added. Narayanan and Zwanziger [17] have rationalized in this way glass formation in alkali-tellurite systems.

3.3.2 Glass Formation Under Hypostatic ($f > 0$) Conditions

This condition is best exemplified by the $x \text{Na}_2\text{O} \cdot (1 - x) \text{SiO}_2$ system where addition of Na_2O leads to conversion of bridging oxygens (with $C = 2$) into non-bridging oxygens (with $C = 1$). The average value of degrees of freedom increases with increase in x :

$$f(x) = \frac{3x}{2 - x}. \quad (7)$$

It is well known that glass formation in alkali-silicate systems becomes difficult for large value of x , especially when $x > 0.5$.

3.3.3 Glass Formation Under Hyperstatic ($f < 0$) Conditions

When $f < 0$, a TD network cannot exist. The excess strain energy can, however, be accommodated in a variety of ways that increase the value of f toward $f = 0$. One possibility is that the network crystallizes, thereby reducing the number of independent constraints by converting some into dependent ones. A second possibility is that new structural units form by breaking weaker constraints. When constraints are broken within structural units, the polyhedra become distorted. The existence of an extended TD network of distorted AB_V polyhedral units (where the BAB angular constraint is broken at the A site but the AB length constraint remains intact) is demonstrated by the example of glass formation in the $\text{CaO-Al}_2\text{O}_3$ binary system. Since neither component is a network former, glass formation in this binary system is poor. If the presence of CaO stabilizes four-coordinated

aluminum ions, Al^{IV} , with two AlO_4 tetrahedra sharing an oxygen vertex (as in silica), then the composition having 50% CaO should be a good glass former. However, experimental results show that glasses in this system form only in a small composition range at about 65% CaO [18]. It is possible to rationalize this observation with the constraint theory. Recently, Jahn and Madden [19] have reported from MD simulations that at 2350 K aluminum is present in Al_2O_3 melt in several different coordination states; about 54% Al^{IV} , 41% Al^{V} , 4% Al^{VI} , and 1% Al^{III} . Further, it was observed that some of the oxygens are present as O^{III} , oxygen coordinated by three aluminums (also known as oxygen triclusters), and the remaining as normal bridging oxygens, O^{II} . One can use this structural information and PCT to rationalize why the 65% CaO composition forms best glasses in this system. First, it can be assumed that the structures of Ca -aluminate and alumina melts are similar except for the incorporation into the network of O from CaO . Next, one can simplify the structural information by neglecting the concentrations of Al^{VI} and Al^{III} . Let z be the fraction of Al^{IV} and $(1 - z)$ that of Al^{V} . Then, for the composition $x \text{CaO} \cdot (1 - x) \text{Al}_2\text{O}_3$, one shows with PCT that the degrees of freedom, f , is given by

$$f(x, z) = \frac{12x + 6z - 6xz - 9}{3 - 2x}. \quad (8)$$

When $f = 0$, Eq. (8) gives the following expression for the isostatic composition x^* [$x(f = 0)$] in terms of z :

$$x^*(z) = \frac{3 - 2z}{4 - 2z}. \quad (9)$$

For $z = 0.54$, Eq. (9) gives $x^* = 0.65$, the same value as for the best glass-forming composition [18].

3.4 Existence of Super-Structural Units

In B_2O_3 glass the presence of rigid, planar boroxol B_3O_6 units made up of three trigonal BO_3 units is well established [20]. In contrast to basic polyhedral units, AB_V , where a single A atom is coordinated by B atoms, *super-structural* units such as boroxol units contain more than one A atom. Do super-structural units then exist in other borate glasses? It is a question that has long persisted in the oxide-glass science.

Super-structural units may be energetically more favorable in systems with long-range interactions. However, their larger size raises difficulties to match the density of networks with the observed density of glass. For example, the boroxol units are topologically equivalent to the basic BO_3 trigonal unit (both have $\delta = 2$ and $V = 3$). If all BO_3 trigonal units in B_2O_3 glass are replaced by B_3O_6 boroxol units, the length scale of the structural unit is doubled (the volume thus increasing by a factor of 8)

while the mass of the unit is only tripled so that the density of a network of boroxol units is only 3/8 of that of a network of trigonal units. Further, based on topological considerations mentioned before, an extended 3-D network can incorporate only a small fraction of super-structural units with $V > 4$. For this reason, the dipentaborate and the di-triborate groups, two of the six super-structural units listed by Wright [20], probably do not exist in significant concentrations.

4 The Bond Constraint Theory

As originally formulated by Phillips [1] for covalent networks, structural units are not considered in BCT. Instead, the system is viewed as a network of atoms at the vertices and covalent linear bonds at the edges. These covalent linear bonds provide $r_i/2$ linear constraints at the i th vertex of coordination number r_i . In addition, there also exist $[r_i(d - 1) - d(d - 1)/2]$ covalent angular-bond constraints at the i th vertex for a d -dimensional network. The average number of constraints, n , per vertex is, therefore,

$$n = \left(\frac{r}{2}\right) + [r(d - 1) - \{d(d - 1)/2\}], \quad (10)$$

where r is the average vertex coordination number. The condition of isostaticity ($n = d$) gives the following value for the critical coordination number r^* (also called the rigidity percolation threshold):

$$r^* = d(d + 1)/(2d - 1). \quad (11)$$

Note that $r^* = 2$ for $d = 2$ and $r^* = 2.4$ for $d = 3$. It must be emphasized that Eqs. (10) and (11) assume that the angular constraints are intact at *every* vertex. This assumption does not always hold true as illustrated by silica where the angular constraints at oxygens are broken, which is generally the case for elements that do not belong to groups III, IV, and V and do not exhibit $\text{sp}^{(n)}$ hybridization.

Application of BCT to non-covalent systems with long-range interactions such as ionic systems is approximate at best, and questionable most of the time, because these systems do not lend themselves to the count of simple nearest-neighbor constraint. For ionic systems, it is thus preferable to use PCT with structural units defined by the radius ratio of cations to anions.

4.1 Self-organization and the Intermediate Phase

Self-organization designates chemical and/or topological rearrangements in a network that take place

spontaneously to reduce the overall energy in the system [21]. An important consequence of this process is that it allows a system to exist as an isostatic network over a range of coordination numbers or compositions. This range is sometimes known as the intermediate phase or reversibility window [22]. The range depends on the system considered and, to some extent, on its thermal history as well as on the property being measured (e.g. enthalpy release during relaxation, Raman frequency shifts in glasses, or activation energy of viscosity). For example, a coordination number range from 2.39 to about 2.52 has been reported for the intermediate phase in $\text{Ge}_x\text{Se}_{(1-x)}$ system from Raman frequency shifts [22], and a range from $r = 2.35$ to about 2.45 in the $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{(1-x)}$ system from enthalpy relaxation [23]. Interestingly, Wang et al. [24] found no evidence of any intermediate phase in the Ge–As–Se system. Also, Shatnawi et al. [25] found no discontinuities or breaks but only smooth variation with respect to composition in the structural response of $\text{Ge}_x\text{Se}_{(1-x)}$ glasses in the range $0.15 < x < 0.40$ implying the absence of any phase transition associated with the start and end of the intermediate phase range.

4.2 Non-bridging Vertices (or Singly Coordinated Atoms)

There has been much discussion in the literature [26] about the role of dangling vertices (or non-bridging nodes) and their influence (if any) on the rigidity characteristics of a network. At least conceptually, it is clear that dangling vertices should not affect the stiffness of the network because they are not network-forming. In this respect, a confusion in the literature exists primarily because of the way constraints and degrees of freedom are counted. Clearly, if a dangling vertex is counted as being part of the network, then it is necessary to count also the length and angle constraints associated with it. A dangling vertex adds three degrees of freedom but also three constraints (one length and two angles), so that it does not make any net contribution to the degrees of freedom in a network if the counting is done correctly. However, the problem is that extra degrees of freedom often appear when the angular constraints of the dangling vertices are not included in the count [26, 27]. Because these extra degrees of freedom are associated with the floppiness of the dangling vertices themselves, they do not influence the rigidity or the flexibility of the underlying network. Thus, the opinion of this writer is that it is best to disregard the onefold coordinated atoms (i.e. dangling or non-bridging vertices) as they have no influence on the rigidity characteristics of a network.

4.3 Glass-forming Ability in Chalcogenide Systems

4.3.1 Ge–Se System

For the binary $\text{Ge}_x\text{Se}_{(1-x)}$ system, the average coordination number $r(x)$ is $(2 + 2x)$ since $r(\text{Ge}) = 4$ and $r(\text{Se}) = 2$, and the system is isostatic at $x^* = 0.2$ (corresponding to the $\text{Ge}_{1/5}\text{Se}_{4/5}$ composition). According to Tichy and Ticha [28], however, the best glass-forming compositions lie on the Se-rich side in the range $0.06 < x < 0.15$. To rationalize this apparent discrepancy, Tichy and Ticha [28] suggested to view the $\text{Ge}_x\text{Se}_{(1-x)}$ system as an extended chemically ordered network of short, linearly-rigid $(\text{Se})_k$ chains containing k seleniums that are cross-linked by Ge atoms. The ends of the Se chains are connected to Ge atoms so that four such chains share a Ge atom. Note that since $x = 1/(1 + 2k)$, k is 2 at $x = 0.2$. A network with $k > 2$ (corresponding to $x < 0.2$) should be floppy ($f > 0$). However, one can show that some of the degrees of freedom (let us denote these by $f^\#$) in such a network for $x < 0.2$ are associated with the dihedral rotation of the inner seleniums ($\text{Se}^\#$), those inside the selenium chains ($-\text{Se}-\text{Se}^\#-\text{Se}-$). A $\text{Se}^\#$ atom can rotate dihedrally about the line joining its two neighboring Se without influencing the deformation pattern of the network (Figure 2). This is one example where certain internal degrees of freedom decouple from the rigidity of the overall network. In another example the extra degrees of freedom associated with a singly coordinated atom (i.e. a dangling vertex) decouple from the rigidity of the overall network. Clearly such decoupled degrees of freedom can be disregarded as far as network rigidity is concerned. The network, therefore, can satisfy the isostaticity condition in the range $x < 0.2$ by forming chemically ordered networks with an appropriate value of the k for the Se-chains. A value of $k = 3$ corresponding to $x = 1/7$ (or about 0.14) is close to the composition where best glass

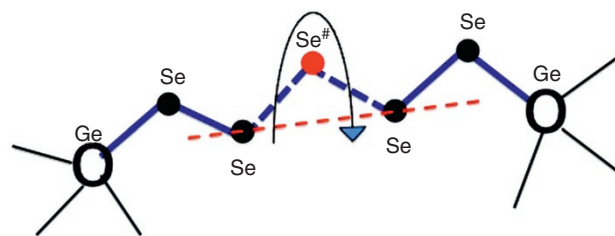


Figure 2 Schematic of a Se-chain with five seleniums connecting two Ge atoms in an isostatic network (not shown). The inner $\text{Se}^\#$ can rotate dihedrally about the dashed line connecting its neighboring seleniums without influencing the rigidity of the network. This dihedral motion of inner seleniums is an internal degree of freedom decoupled from the rigidity of the overall network.

formation is observed, explaining why good glass formation takes place for $x < 0.15$.

For $x > 0.2$, there is experimental evidence for edge-shared GeSe_4 tetrahedra [29]. Because the presence of edge sharing does not change the value of r , the BCT results are not affected but edge sharing does cause differences in the intermediate-range topology. When one considers a pair of edge-shared tetrahedra as a single unit with four Se vertices (and two internal Ge atoms), such a bi-tetrahedral unit has an internal degree of freedom, namely rotation about the shared edge. This additional flexibility allows isostaticity to hold beyond the GeSe_2 composition ($x = 1/3$) in the PCT formalism even though the BCT results do not change. It is also clear that the presence of Ge–Ge homopolar bonds [16] – that must exist for $x > 0.33$ – does not influence the short-range topology of the network. Hence, the BCT consequences do not change.

4.3.2 As–Se System

Since $r(\text{As}) = 3$ in the $\text{As}_x\text{Se}_{(1-x)}$ system, $r^* = 2.4$ corresponding to $x^* = 0.4$. But good glass formation has been observed in the Se-rich range from $x \sim 0$ to $x \sim 0.23$. As in the Ge–Se system, this discrepancy can be rationalized by viewing the As–Se glasses for $x < 0.4$ as a chemically ordered network made up of linearly-rigid (Se_k) short chains, three of which being connected to every As atom. If one eliminates the internal degrees of freedom associated with the dihedral rotations of $\text{Se}^\#$ in the Se chains, it follows that these chemically ordered $\text{As}((\text{Se})_k)_{3/2}$ systems are isostatic for $x \leq 0.4$. Note that since $x = 2/(2 + 3k)$, $k \geq 2$ corresponds to $x \leq 0.25$, which fits well the reported composition range for good glass formation [28].

4.4 Composition Variation of Properties in Glass-forming Systems

Most properties of glasses exhibit rather uninteresting monotonic continuous variations even when r crosses its isostatic value. Only some configurational properties show extremum values with respect to r at the rigidity percolation threshold (i.e. at $r^* = 2.4$). Tatsumisago et al. [30] reported that the configurational heat capacity and the activation energy of viscosity exhibited minima in the Ge–As–Se system at $r = 2.4$. Similar results were obtained by Senapati and Varshneya [31] in the Ge–Se and Ge–Sb–Se systems. It is worth noting that by investigating a range of Ge–As–Se compositions, all having the same values of r , Wang et al. [24] have reported that values of the configurational properties are not a unique function of r implying that topology alone is not sufficient to determine the variation of properties with composition, effect of chemical disorder must also be considered.

5 Temperature-Dependent Constraints

5.1 The Influence of Thermal Energy

Implicit in the original PCT and BCT theories was the notion that constraints are fixed for good – either intact ($= 1$) or broken ($= 0$) – and that they do not vary with temperature (T). Thermal energy was implicitly neglected in the original theories which were thus valid only at $T = 0$ K. To remedy this problem, Gupta [5] introduced the concept of a T -dependent bond constraint. He argued that, if E_i is the energy of a certain class of bonds, then the value of the corresponding constraint $h_i(T)$ should be expressed by a Boltzmann expression:

$$h_i(T) = 1 - \exp\left(-\frac{E_i}{k_B T}\right), \quad (12)$$

where k_B is the Boltzmann constant. Note that the value of h_i always lies in the interval $[0,1]$, being zero in the high-temperature limit, equal to 1 at sufficiently low temperatures, and decreasing monotonically with increasing T . Physically, a fractional value of a bond constraint means that only a fraction of i th type of bonds are intact at a given instant. One may associate a characteristic temperature T_i for the i th type of constraint as follows:

$$T_i = \frac{E_i}{k_B \ln 2}, \quad (13)$$

so that this constraint can be considered effectively as broken ($= 0$) for $T > T_i$ and intact ($= 1$) for $T < T_i$. For both stretching and bending constraints, this formalism has been validated by comparisons of the standard deviations of the partial distributions calculated for glassy and crystalline alkali disilicates as a function of temperature in MD simulations [9].

The average degree of freedom per vertex, $f(T)$, in the network thus becomes T -dependent and (for $d = 3$) is given by

$$f(x, T) = d - \sum_i n_i(x) h_i(T). \quad (14)$$

Since h_i is a decreasing function of T , $f(T)$ always increases with temperature.

5.2 Extension of the Topological Constraint Theory to Supercooled Liquids

In 1999, Gupta [6] extended the notion of T -dependent bond constraints to glass-forming supercooled liquids: “*Since the structure of a glass formed by cooling a liquid is the same as the structure of the liquid at the glass transition (or fictive) temperature, T_g it follows that if the glass structure is an extended TD network, then such a network*

must also exist in the super-cooled liquid state at T_g ." More importantly, he argued that the configurational entropy, $\Delta S(T)$, of a supercooled liquid is approximately proportional to the average degrees of freedom per vertex, $f(T)$. This result, later substantiated by Naumis [32], leads to several important consequences:

- a) At the Kauzmann temperature, T_K , defined by $\Delta S(T_K) = 0$, the degrees of freedom vanish:

$$f(T_K) = 0. \quad (15)$$

- b) From the Adam–Gibbs theory of viscosity, it follows that the temperature-dependence of viscosity is simply related to that of $f(T)$:

$$\ln \eta(T) = \ln \eta(\infty) + \frac{A}{T f(T)}. \quad (16)$$

Here, A is a constant independent of T .

- c) The fragility, m , of a liquid defined as

$$m \equiv \frac{1}{T_g} \left[\frac{\partial \log_{10} \eta}{\partial (1/T)} \right]_{T=T_g}, \quad (17)$$

is related to the temperature-dependence of f as follows:

$$m \equiv \left[\log_{10} \frac{\eta_g}{\eta_\infty} \right] \left[1 + \frac{\partial \ln f}{\partial \ln T} \right]_{T=T_g}. \quad (18)$$

The value of $\log [\eta_g/\eta_\infty]$ is about 16. The variation of the degrees of freedom, $f(T)$, with T , for good, poor, and non-glass-forming liquids is shown schematically in Figure 3. From Eq. (16), one then concludes that the cause of the non-Arrhenian nature of the viscosity is the temperature-dependence of bond constraints.

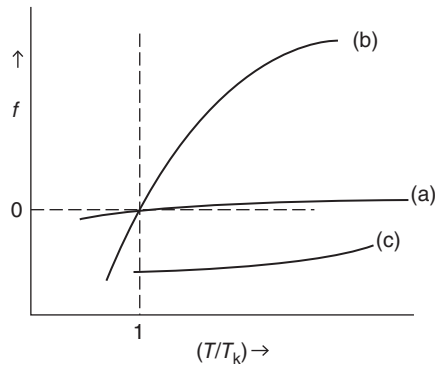


Figure 3 Schematic variation of degrees of freedom (f) in three supercooled liquids with increasing temperature normalized with respect to the Kauzmann temperature (T_K). Curve (a) represents a strong glass former, curve (b) a fragile glass former, and curve (c) a non-glass former for which a TD network cannot exist (Source: From [6]).

5.3 Temperature – Scaling of Viscosity (η) and the MYEGA Equation

Substituting Eqs. (12) and (14) in Eq. 16 and assuming that only one type of constraints (with n constraints per vertex) varies within the temperature range of interest, one obtains the following temperature scaling of viscosity for supercooled liquids:

$$\ln \eta(T) = \ln \eta(\infty) + \frac{A}{T[(3-n) + n \exp(-E/k_B T)]}. \quad (19)$$

For deeply supercooled liquids in the vicinity of the glass transition, n is approximately equal to 3 and Eq. (16) simplifies to

$$\ln \eta(T) = \ln \eta(\infty) + \frac{B}{T} \exp\left(\frac{E}{k_B T}\right), \quad (20)$$

where B is a new constant. This Eq. (20) is the well-known MauroYue-Ellison-Gupta-Allan (MYEGA) expression [33] for the T -dependence of the equilibrium viscosity, which has been remarkably successful in fitting the experimental data on the T -dependence of viscosity for a large number of inorganic and organic liquids. It should be noted that, like the Vogel-Tammann-Fulcher (VFT) equation, the MYEGA has only three fitting parameters but, unlike VFT, it does not exhibit any divergence of viscosity at any finite temperature.

5.4 The Composition Variation of the Glass Transition Temperature, T_g

If the value of the parameter A in Eq. (16) has a negligible composition dependence, then it follows from this equation that

$$T_g(x)f[T_g(x)] = T_g(x_{\text{ref}})f[T_g(x_{\text{ref}})] = \text{const.} \quad (21)$$

Here, x_{ref} is a reference composition. The importance of Eq. (21) cannot be overstated. It provides a means of modeling the composition dependence of T_g from the knowledge of the atomic level short-range order as a function of composition. Traditionally, such information on the short-range order has been obtained from X-ray or Neutron diffraction studies. Nowadays, such information can also be obtained accurately using MD studies.

Gupta and Mauro [7] used the T -dependent constraint theory to rationalize quantitatively the variation of the glass transition temperature, $T_g(x)$, with composition in the binary $\text{Ge}_x\text{Se}_{(1-x)}$ chalcogenide system. Their analysis resulted in the modified Gibbs–DiMarzio equation:

$$T_g\left(0 \leq x \leq \frac{1}{3}\right) = T_g(0) \left[\frac{1}{1 - (ax)} \right], \quad (22)$$

with a value of the parameter $\alpha = 5/3$, which is the value observed experimentally [31]. In addition, using Eq. (18), Gupta and Mauro [7] were also able to explain the variation of the fragility, m , as a function of composition.

Mauro et al. [8] later applied the T -dependent constraint theory to binary alkali-borate systems where a wealth of structural information is available as a result of years of X-ray diffraction and NMR spectroscopy

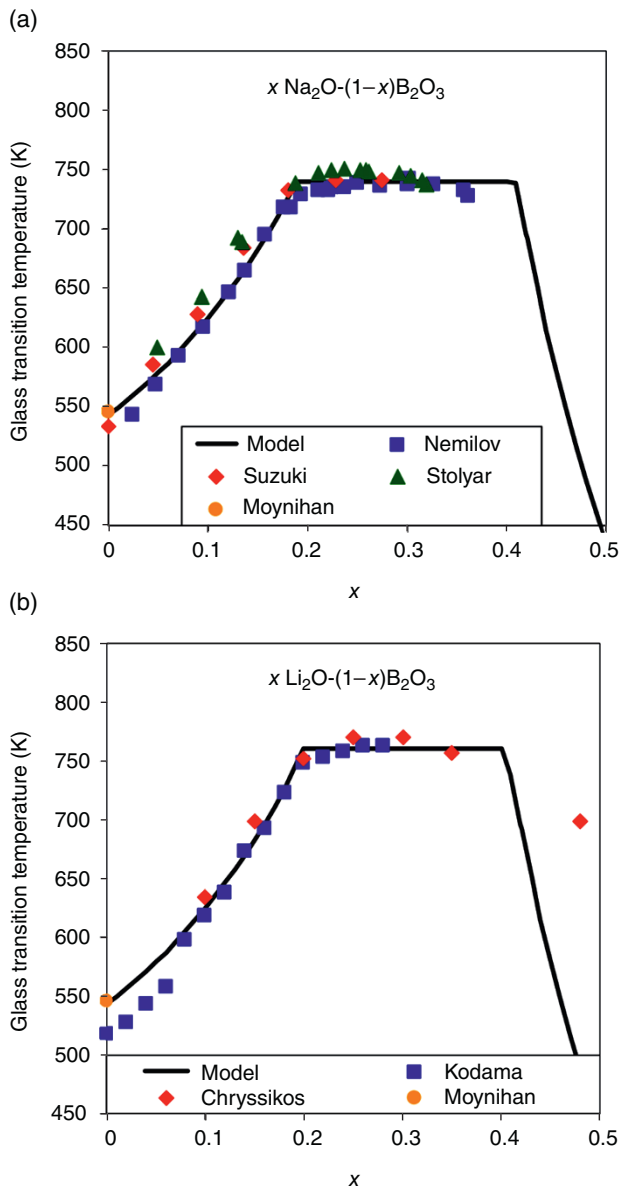


Figure 4 Composition dependence of the glass transition temperature for the (a) sodium borate and (b) lithium borate systems. Solid curves: predicted $T_g(x)$ using the temperature-dependent TCT. Points: experimental data (Source: From [8]).

experiments. The agreement for both T_g and m between TCT and experimental results is remarkable considering that only one fitting parameter was used for all the data (see Figures 4 and 5). Using a similar approach, Smedskjaer et al. [34] have successfully extended the T -constraint theory to ternary system $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3$ system. In 2011, they also analyzed the four component $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$ system [10].

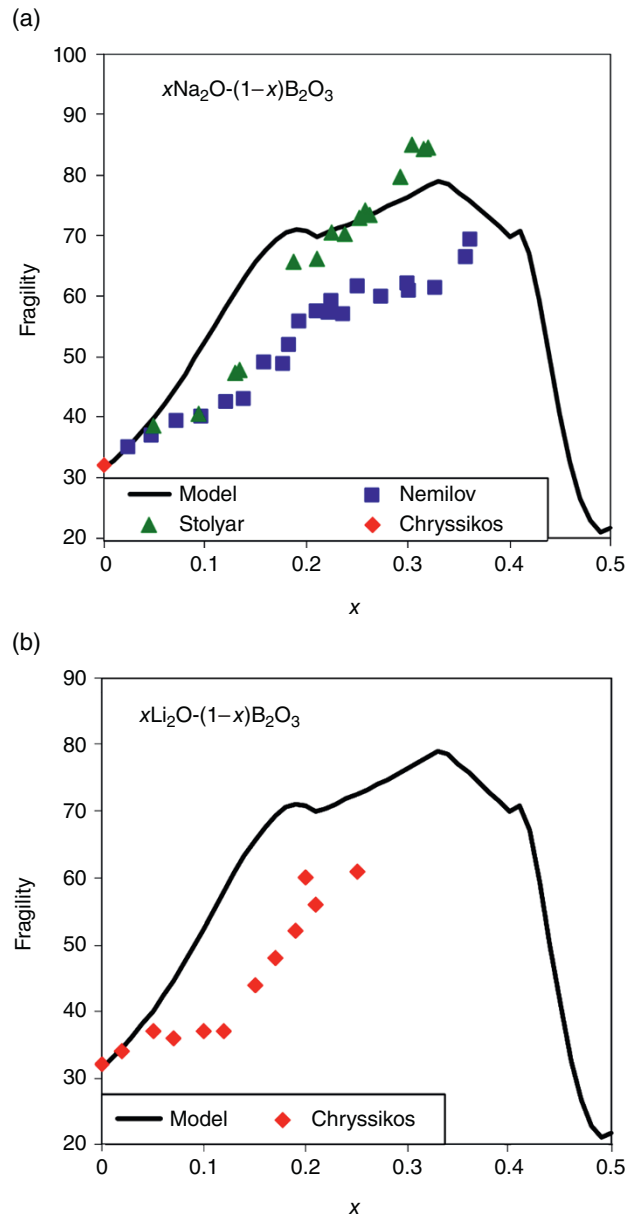


Figure 5 Variation of fragility with composition in the (a) sodium borate and (b) lithium borate systems. Curves calculated with the T -dependent TCT. The step increase in fragility around $x = 0.2$ is a consequence of a fragility transition in these systems (Source: From [8]).

5.5 Fragility (or Rigidity) Transitions and Iso- T_g Regimes

A generalized T -dependent activation energy, $H(T)$, is defined as the slope of the Arrhenius plot of viscosity:

$$H(T, x) = k_B \frac{\partial \ln \eta}{\partial (1/T)}. \quad (23)$$

The ratio, $H(T_g, x)/(k_B T_g)$, is proportional to the fragility m . In some systems, the activation energy (or fragility) shows rounded discontinuities as a function of T or as a function of composition, X . These jumps are referred to as fragility transitions. An example of such transition in the alkali-borate systems is shown in Figure 5. Fragility transition as a function of temperature for a fixed composition is illustrated in Figure 6. In a temperature-induced fragility transition, a system always becomes more fragile at higher temperatures simply because more constraints are broken as the temperature is increased.

Mauro et al. [8] made an interesting observation in the binary alkali-borate melt $x\text{M}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ systems where T_g appears to be a constant function of composition for a small composition range. They called this composition range the “iso- T_g regime” (Figure 4). The iso- T_g step results when a bond constraint breaks exactly at T_g . It can be shown that, within the iso- T_g regime, the fragility remains constant and equal to the low value of about 16 that is observed for strong glasses. Interestingly, the composition range of the iso- T_g regime (at least in the alkali-borate system) is nearly the same as that of the reversibility window observed by Boolchand and colleagues [22]. This coincidence raises the possibility of some connection between the two phenomena, an area that requires further investigation.

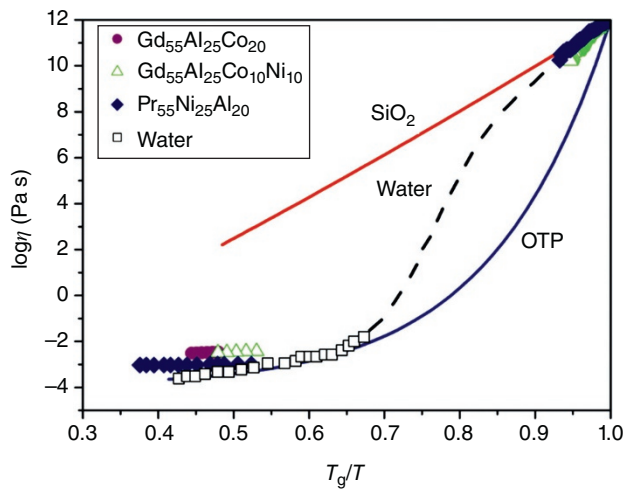


Figure 6 Contrast between strong (SiO_2) and highly fragile (O-Terphenyl, OTP) in plots of viscosity against reciprocal temperature, and intermediate cases of liquids fragile at high temperatures and becoming strong at low temperatures (water, glass-forming metals) through a diffuse transition (cf. Chapter 3.8; Source: From [35]).

6 Topological Constraint Theory, Thermodynamics, and the Potential Energy Landscape Formalism

The impressive applications of TCT demand answers to fundamental questions such as how is TCT connected to the thermodynamics of liquids and glasses and how to formulate TCT from the first-principles statistical physics of potential-energy landscapes of liquids and glasses. This is an area that has not received much attention so far except for the work of Naumis and coworkers [13, 32] that we summarize in this section.

Naumis uses simple harmonic potentials to express the Hamiltonian (H) of a floppy system as follows:

$$H = \sum_1^{3N} \frac{p_j^2}{2m} + \sum_1^{3N(1-x_f)} \frac{1}{2} m \omega_j^2 q_j^2 + \sum_1^{3Nx_f} \frac{1}{2} m \omega_o^2 q_j^2. \quad (24)$$

Here, x_f is the fraction of floppy modes ($= f/3$); p_j and q_j are, respectively, the momentum and position coordinates of oscillators representing vibrational modes of frequency ω_j and floppy modes of frequency ω_o . For real systems, one has to use more sophisticated interaction potentials. Nonetheless, a harmonic model gives a reasonable qualitative feel of the thermodynamics of the floppy modes. Naumis assigns a small but finite frequency ω_o ($< \omega_{\text{vib}}$) to each floppy mode. The equilibrium thermodynamics of this Hamiltonian can be calculated easily. The result for the internal energy U of the system is

$$U(T) = (3-f)NkT D\left(\frac{\hbar\omega_D}{kT}\right) + fN \left[\frac{\hbar\omega_o}{\exp\left(\frac{\hbar\omega_o}{kT}\right) - 1} \right]. \quad (25)$$

Here, D is the well-known Debye function and ω_D is the Debye frequency. According to Naumis, the expression for entropy is as follows:

$$S(T) = k \ln \left[\left(\frac{12\pi kT}{h} \right)^{N(3-f)} \prod_1^{N(3-f)} \left(\frac{1}{\omega_j} \right) \right] + Nf k \ln \left(\frac{12\pi kT}{h\omega_o} \right). \quad (26)$$

The last terms in Eqs. (25) and (26) represent the contributions of the floppy modes and constitute the configurational energy and entropy, respectively. As discussed in Section 5.2, the configurational entropy is proportional to f .

From Eq. (25), the configurational heat capacity, ΔC_V , is given by

$$\Delta C_V = fNk \frac{x^2 e^x}{[e^x - 1]^2} + NkT \left[\frac{x}{e^x - 1} \right] \left(\frac{\partial f}{\partial T} \right), \quad (27)$$

where $x = h\omega_o/kT$.

As Naumis has pointed out, the physical picture in the PEL is clear. Since ω_o is small, the curvatures of the potential energy surface at the inherent structures are small in the floppy directions. Naumis refers to these directions as channels in the landscape. The landscape is flatter in these channels, thus allowing greater configurational entropy and greater structural freedom upon increase in T and thus greater fragility.

7 Perspectives

Over the last 25 years, TCT has evolved from theoretical inquiries about the existence of Zachariasen's TD networks and easy glass formation in simple systems to a widely used scheme for modeling variations of properties with composition in multicomponent glasses and glass-forming liquids. The trends predicted by TCT are in good agreement with experimental results. This is largely because TCT takes as input the observed or modeled variation of topology with composition and a fundamentally sound temperature-dependence of chemical bond strengths. In this sense, TCT represents a major leap in the development of science-based engineering of new glass compositions.

In spite of its success, several limitations and fundamental issues remain unresolved. We list some of these here.

- 1) For systems with short-range interactions where BCT is applicable, it is unclear when to treat the angular constraints as broken (even at low temperatures). For example, why is the angular constraint broken at oxygens in silica? Are they broken at Se in selenides? It appears that angular constraints are intact primarily in group III, IV, and V elements that exhibit $sp^{(n)}$ hybridization. Clearly, a more detailed understanding of the basis of the angular constraints will lead to more accurate predictions of BCT.
- 2) Extension of TCT to systems with long-range potentials (especially ionic interactions) remains vague and questionable at present. Whereas BCT applies only to systems with short-range covalent interactions, PCT works better for ionic systems. The effects of chemical order in BCT and of chemical disorder in PCT need further examination. There is a clear need for a more fundamental basis for applying TCT to chemically disordered systems having long-range interactions.
- 3) It has been noted that the rigidity percolation threshold may not occur at a single composition, but over a range of compositions because of either localization of constraints or localization of degrees of freedom in an

otherwise isostatic matrix. Whereas a discussion of iso- T_g range is presented, there does not exist at present a theory to determine the rigidity percolation composition range.

- 4) The role of intermediate-range topology (ring-size distribution) in determining the deformation of a network remains unclear. For example, edge-sharing between tetrahedra in the Ge-Se system appears to have no effect on the BCT results since both edge and corner sharing give rise to identical short-range topology (i.e. the same value of r).
- 5) Whereas an approximate relation between configurational entropy and degrees of freedom has been discussed, a more rigorous understanding of constraints (or degrees of freedom) in general in terms of features of the PEL is needed to embed the TCT in the general statistical physics of the disordered condensed state.
- 6) The minimum free-energy configuration in the supercooled liquid state corresponds to the most probable network configuration. Thus, a relationship between the free energy of the supercooled liquid and the nature of constraints is expected. Establishment of such a relationship will provide a sound thermodynamic foundation of TCT and will provide answers to the important questions as to why good glass-forming compositions are also low-temperature eutectics.
- 7) All systems have configurational fluctuations at a finite temperature. The present formulation of TCT applies only to the average network configuration so that the influence of fluctuations is not accounted for. Clearly, extension of TCT to include configurational fluctuations is desirable to model fluctuation-based properties.

In spite of these limitations, it is important to emphasize that the success of TCT in some systems has been remarkable. But with increasing need to apply TCT to a large variety of systems, it is necessary to develop a theoretically sound basis to resolve these issues.

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2.8

Atomistic Simulations of Glass Structure and Properties

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1 Introduction

Following Zachariasen's epoch-making *continuous random network* (CRN) model [1], the first generation of atomistic models of glass relied on craft construction of ball-and-stick representations of atomic structures. Perhaps the most successful model was constructed for SiO_2 glass by Bell and Dean [2] who patiently assembled manually rods and balls to compose 188 tetracoordinated units with a total of 614 atoms. The disordered linkage of the SiO_4 groups, which were assumed to be rigid, did satisfy Zachariasen's structural rules.

From the angles and distances they measured, Bell and Dean also determined the pair distribution functions (PDF) for Si–Si, Si–O, and O–O, from which they derived a radial distribution function (RDF) that was in good agreement with the experimental data over their full range of definition, i.e. out to a distance of about five times the Si–O bond length. Yielding in particular an average O–Si–O bridging angle of 153° , this model enabled the three-dimensional atomic configuration of SiO_2 glass to be visualized, but it suffered from an obviously large arbitrariness in its handmade combination of building blocks. In addition, the model did not lend itself to estimations of physical properties. An exception was the density, which was calculated for an internal portion of the model system consisting of 72 SiO_2 units, to yield a value of 1.99 g/cm^3 that proved to be much lower than the actual 2.20 g/cm^3 .

Atomistic simulations have rendered such mechanical models obsolete as they readily provide not only atomic coordinates but also predict physical properties for glass

and melts of any composition under a variety of temperature, pressure, or energy conditions. Besides, the accuracy and versatility of these calculations have been improving steadily, thanks to faster computing processors, more efficient algorithms, and bigger systems investigated. Originally, these simulations were mainly developed to give exact solutions to problems in statistical mechanics which would otherwise have been intractable for complex states of matter such as liquids, glasses, or aggregates.

The first simulations were made with the Monte-Carlo (MC) method (e.g. [3]), which had been devised in the 1930s to solve general mathematical and statistical problems. It took advantage of the first electronic computers to sample the configurations of the system according to Boltzmann statistics, and weight them evenly when calculating the associated properties of interest. Because of this reliance on Boltzmann statistics, however, only equilibrium states can be investigated in MC simulations. At the cost of much computational complexity, the advantage of molecular dynamics (MD) simulations (e.g. [4]) is to characterize at every moment the state of the system by the positions and momenta of its constituting atoms and, thus, to account for the dynamics of the system whether in equilibrium or not. For SiO_2 , the first MD simulation performed by Woodcock et al. [5], for instance, dealt with the anomalous properties of the melt and assigned increases in diffusion coefficients to pressure-induced structural changes. Following this pioneering study on a real material, a great many MD simulations have been carried out on glass/melt systems since that time.

Interatomic potentials are critical ingredients in both MC and MD simulations (e.g. [4]). As a preamble, it is thus appropriate to begin this chapter with a brief review of the manner in which they are determined within the general framework of numerical simulations. The principles of MC and MD simulations will then be

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presented. Finally, simulations made on amorphous oxide glasses will illustrate the interest and diversity of results that can be obtained with MD simulations and their complementarity with those of experimental studies. Amorphous SiO_2 , silicates, or phosphates will be mentioned but special interest will be paid to the structure of B_2O_3 glass that actually represents stringent tests of simulations as it requires accurate descriptions of both short- and medium-range order to be understood. Other important applications of atomistic simulation to transport properties are discussed in Chapter 4.6.

2 Basics of Numerical Simulations

2.1 General Features

Atomistic simulations rely on statistical mechanical models. As such they may be performed within three main kinds of statistical ensembles. The canonical NPT ensemble (constant number of atoms, pressure, and temperature) is chiefly used in heating or quenching cycles. In contrast, the micro-canonical NVE ensemble (constant number of atoms, volume, and energy) is primarily used when properties are calculated within the precise framework of statistical mechanics. As for the grand canonical μVT ensemble (constant chemical potential, volume, and temperature), it is typically used to investigate chemical equilibrium in systems that can exchange energy and matter with a reservoir.

For an isolated macroscopic system made up of a very large number N of atoms, each having three degrees of freedom, the microscopic state at a given instant is completely specified by the values of $3N$ coordinates $r(i)$, collectively denoted by r^N , and $3N$ momenta $p(i)$, denoted similarly by p^N . The values of the variables r^N and p^N define a point in a $6N$ -dimensional space, called the phase space, symbolized by Γ_N . If $H(r^N, p^N)$ is the Hamiltonian of the system, the path followed by this point in the phase space is determined by Hamilton's equations:

$$\dot{r} = \frac{\partial H}{\partial p(i)} \quad (1)$$

$$\dot{p} = -\frac{\partial H}{\partial r(i)}, \quad (2)$$

where $i = 1, \dots, N$. In principle, $6N$ coupled equations subjected to $6N$ initial conditions should be solved to specify the values of all $r(i)$ and $p(i)$ at a given time.

The first difficulty encountered is that the timescale of microscopic processes is ultimately controlled by the 10^{-14} – 10^{-15} second period of atomic vibrations. In atomistic simulation, a time integration with similar discrete steps thus is required to describe accurately the time

evolution of a system. Even with today's most powerful computers, this constraint restricts simulations to low-viscosity conditions at which relaxation times (cf. Chapter 3.7) are lower than about 10^{-6} seconds to be consistent with the calculational time steps.

It follows that the glass transition cannot be investigated as a number of calculation steps of the order 10^{18} would be required to deal with a relaxation time of $\sim 10^3$ seconds. Likewise, crystal nucleation and growth or liquid–liquid phase separation take place too slowly to be subjected to atomistic simulations. Besides, simulated melts are quenched at cooling rates at least six orders of magnitude faster than the highest rates of $\sim 10^6$ K/s achievable practically. The fictive temperatures of the simulated glasses that then be up to 1000 K higher than those of real glasses, which one should keep in mind when making any kind of comparison between both kinds of materials.

Besides, a second difficulty stems from the fact that N is of the order of the Avogadro number (6.02×10^{23}) for any macroscopic system. Experience shows, however, that accurate results can be obtained for systems of only a few hundred or thousand atoms as long as structural units bigger than the system itself are not involved in the processes investigated. To avoid either creating surface or setting up a wall (Figure 1), periodic boundary conditions are usually imposed in numerical simulations. The cubic box is replicated throughout space to form an infinite lattice. As an atom moves in the original box, its periodic image in each of the neighboring boxes moves in exactly the same way. As an atom leaves the central box, one of its images will enter through the opposite face.

To simulate accurately a noncrystalline configuration in the cell, a larger number of atoms are nonetheless preferable. When a small cell of around several hundred atoms is studied, periodic boundary conditions, for

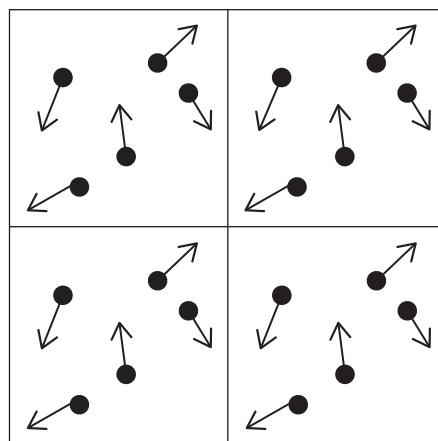


Figure 1 Schematic representation of periodic boundary conditions.

instance, prevent structural units larger than the cell from forming. As already alluded to, any structural unit or spatial fluctuation larger than the wavelength which is greater than half of the cell size cannot be calculated appropriately because the repeatedly arranged fragments would be involved in the results. On the other hand, the maximum number of atoms which can be currently processed is of the order of 10^5 – 10^6 . To check whether the number of atoms or the size of simulation cell is sufficient or not, the best way is to double the number of atoms and to maintain the same density through an adjustment of the cell size and then to make sure that there is little change in the calculated structural data.

2.2 The Importance of Interatomic Potentials

Strictly speaking, in numerical simulations the Hamiltonian should be calculated from the quantum wave-function equation, $H\psi = E\psi$, where ψ and E are the wave-function and energy of the system, respectively. As expounded in Chapter 2.9, such calculations require so much computing work that they are currently restricted to smaller systems typically made up of a few tens of atoms. In the present chapter, simulations made within a classical framework will thus be considered instead. They rely on the fact that the differences between vibrational and electronic energies and frequencies are so large that atomic vibrations may be considered to take place within a fixed electronic configuration. This is the celebrated Born–Oppenheimer approximation whereby the Hamiltonian of a system is expressed as the sum of kinetic and potential energies, which are functions of the selected set of coordinates $q(i)$ and momenta $p(i)$:

$$H(p, q) = K(p) + U_p(q). \quad (3)$$

In Eq. (3) the kinetic energy, $K(p)$, is simply expressed as a function of the mass and of the velocity calculated for each atom. The potential energy, $U_p(q)$, is much less readily determined because it strongly depends on the specific interactions between the various kinds of atoms present in the system. Quite generally, however, interaction potentials are markedly asymmetrical in terms of interatomic distances because they rise extremely steeply when atoms get mutually very close whereas they reach a constant value – the dissociation energy – when atoms become so distant that they can be considered as no longer bonded. As introduced in 1929 to represent isolated diatomic molecules, the Morse potential accounts well for this asymmetry:

$$U_p(r_{ij}) = E_0 \left[\left\{ 1 - \exp(-k(r_{ij} - r_0)) \right\}^2 - 1 \right], \quad (4)$$

where E_0 , k , and r_0 are the dissociation energy, a measure of the bond strength, and the equilibrium interatomic distance of the molecule, respectively, three parameters that are determined from vibrational spectroscopy data.

In a condensed phase, potentials are much more complicated since a given atom interacts with a great many others over distances that can be large. To keep the number of parameters as small as possible in the expression of potential energies, one thus groups into the same term all interactions between given pairs of like or unlike atoms regardless of their mutual distances. Although the Morse potential remains a good starting point for systems where bonding is covalent, other kinds of analytical expressions are generally used for potential energies in the MC and MD simulations dealt with in this chapter. As borne out by the variations with composition of macroscopic properties, atomic interactions have the simplifying feature that they are primarily pairwise in oxide or salt systems. This feature is embodied in the most popular potentials used for these systems, namely, the Buckingham,

$$U_p(r_{ij}) = A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}, \quad (5)$$

and the Born–Mayer–Huggins potentials,

$$U_p(r_{ij}) = A \exp[B(r_{ij} - r_0)] - \frac{C}{r_{ij}^6} - \frac{D}{r_{ij}^8}, \quad (6)$$

where r_{ij} is the distance between two atoms, and A , B , r_0 , C , D are parameters inherent to each interaction (Figure 2).

In both potentials, the first, second, and third terms represent repulsive interaction, dipole–dipole dispersion, and dipole–quadrupole dispersion, respectively. In more precise formulations, ternary and higher-order effects must be accounted for so that the potential energy is made up of terms depending on the coordinates of individual atoms, pairs, triplets, etc.

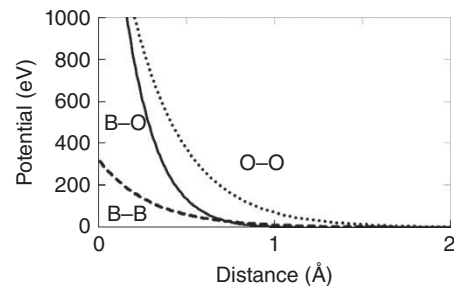


Figure 2 Examples of potential energy models: Morse and Buckingham potentials used in B_2O_3 simulations for B–O and for O–O and B–B, respectively [6].

$$U_p = \sum_i u_1(r(i)) + \sum_i \sum_{j>i} u_2[r(i), r(j)] + \sum_i \sum_{j>i} \sum_{k>j} u_3[r(i), r(j), r(k)] + \dots \quad (7)$$

The first term u_1 is discarded in standard simulations because it accounts for external fields (i.e. wall, electrical field, gravity, magnetic field, and centrifugal force). The second term u_2 is the most important since it represents the relevant pair potentials. When determined empirically, it actually includes three-body and many-body effects, which is why models relying on simple pair potential model reproduce reasonably well liquid or glass structures, and why it is better in this case to denote it by the term “effective” pair potential.

As illustrated by Eq. (7), empirical potentials have a great flexibility since specific terms may be added if needed. When electrostatic interactions are important, a Coulomb charge–charge interaction may, for instance, be included in the form:

$$U_{zz}(r_{ij}) = \frac{z_i z_j}{4\pi\epsilon_0 r_{ij}}, \quad (8)$$

where z_i, z_j , and ϵ_0 are the charge on atom i and j and the permittivity of free space. Because the Coulombic series converges very slowly, the Ewald, particle-mesh, or multi-pole techniques are used in periodic systems. Likewise, more complex models implement three- and four-body terms to reproduce bond-bending and torsional forces, respectively. Alternatively, polarizable or shell models are employed to consider ions as nonrigid entities and, thus, to account for the effects of the deformation of electron clouds with suitable additional parameters.

From a practical standpoint, the parameters of equations such as (4–7) can be estimated in two different ways depending on the nature of the data to which they are fitted [4]. In the most rigorous way, one relies on energy profiles determined in first-principles calculations or quantum-mechanical simulations of appropriate reference systems (cf. Chapter 2.7). Alternatively, potential energy parameters are fitted through MD or lattice dynamics calculations to some selected physical properties. Structural and elastic data are generally chosen because they are most directly related to interatomic potentials. Thermal properties may also be used, but they are sensitive to second-order effects such as anharmonicity and are in turn generally predicted less accurately.

3 Monte-Carlo Simulations

3.1 Principles of the Method

First described for atomistic simulations in 1953 by Metropolis et al. [7], the MC method cannot account

for the time evolution of the system investigated. By calculating instead its physical properties from repeated samplings made on the basis of a Boltzmann energy distribution of equilibrium states, it differs from a search algorithm with which the energy of the system would occasionally increase even though a steady decrease would be sought after at every step. As already stated, the method is thus inappropriate to tackle any nonequilibrium or history-dependent phenomenon. Over MD simulations, its main advantage is to shorten the calculation time needed to arrive at the equilibrium structure if a suitable sampling method is employed.

Within the framework of the canonical ensemble, the partition function $Q(N, V, T)$ is, for example,

$$Q(N, V, T) = \frac{1}{((\Lambda^3)^N N!) \int d\mathbf{r}^N \exp[-\beta U_p(\mathbf{r}^N)]}, \quad (9)$$

where $\Lambda = \sqrt{h^2/(2\pi m k_B T)}$ is the thermal de Broglie wavelength, β the reciprocal temperature ($1/k_B T$), and $N, \mathbf{r}, U_p, m, k_B$, and T are the number of atoms, atomic coordinates, potential energy of a system, atomic mass, Boltzmann’s constant, and temperature, respectively.

From the partition function it follows that the probability (P) of finding a configuration $\mathbf{r}^N$ is

$$P(\mathbf{r}^N) \propto \exp[-U_p(\mathbf{r}^N)]. \quad (10)$$

To fulfill Eq. (9), the standard Metropolis procedure in MC simulations consists of

- 1) setting up an initial configuration in a periodic boundary cell,
- 2) calculating the energy of this configuration,
- 3) selecting an atom at random and moving it randomly along all coordinate directions,
- 4) accepting the new configuration resulting from the move if it lowers the energy of the system, because the new state is more probable than the former, but keeping the former configuration otherwise only in case its Boltzmann factor is higher than a real number drawn randomly between 0 and 1.

In other words, the MC method does not weight configurations selected randomly according to their Boltzmann factor to calculate the properties of the system, as was done earlier, but weight evenly instead configurations selected with the probability $\exp[-U_p(\mathbf{r}^N)]$. Its trick thus is to concentrate on the sampling in the regions of the phase space that contribute the most to the partition function. Although they will not be described here, there are several other sampling methods in the standard MC calculations to accelerate convergence to the equilibrium state [3].

3.2 Reverse Monte-Carlo Simulations

To complement standard MC simulations, the so-called reverse Monte-Carlo (RMC) method has been developed to study disordered structures [8]. It enables three-dimensional structural models to be constructed in a manner consistent with experimental results. The data most commonly used are PDF and their Fourier transforms obtained from diffraction experiments (Chapter 2.2). In RMC calculations the standard procedure is to

- 1) set up an initial configuration in a periodic boundary cell,
- 2) calculate the set of quantities relevant to the experimental data considered (e.g. PDF),
- 3) calculate the mean square deviations χ^2 of the calculated from the observed results

$$\chi^2 = \frac{\sum (y_{\text{obs}} - y_{\text{cal}})^2}{\rho^2}, \quad (11)$$

where ρ is an appropriate measure of experimental accuracy,

- 4) select an atom and give it a random displacement,
- 5) accept the move if it leads to a χ^2 decrease, but keep the former configuration otherwise,
- 6) repeat from 2) to 5).

To quote a single example, the structural role of “insufficient” network formers has been successfully studied by RMC in a simulation of the atomic configuration of Mg_2SiO_4 glass in which the measured total structural factors were well fitted [9]. The estimated bond distance of

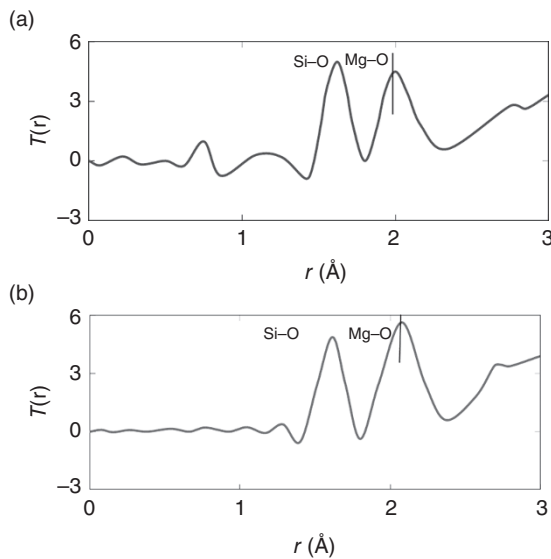


Figure 3 As defined by Eq. (20), total correlation functions $T(r)$ of Mg_2SiO_4 glass (a) and crystal (b) [9].

Mg-O differs in the glass and in the crystal (Figure 3), whereas the difference in the peak position of Mg-O between the two phases reflects the structural feature the glass network is built by the corner- and edge-sharing of highly distorted Mg-O -bearing species.

The advantage of the RMC method is that knowledge of interatomic potentials is not required, but its drawback is that it is not applicable to novel glass systems for which no experimental data can be compared with model values. Besides, there is a risk of arriving at an incorrect structure if the iterative procedure leads to a local, and not to the true minimum of χ^2 . A simple way to avoid such a pitfall is to add a set of effective constraints on bond lengths, bond angles, or coordination numbers (CN) that will prevent spurious results from being obtained.

4 Molecular Dynamics Simulations

The main advantage of MD simulation is to provide important structural information that complements conclusions drawn from experimental studies. One such important result was the demonstration that the structure of sodium silicate glasses fits the modified random network model because the spatial distribution of sodium ions showed a clustering tendency [10]. The result was especially significant as the extremely high fictive temperatures of glasses quenched in MD simulations strongly favor a much more random distribution.

For such reasons, MD simulations have become the most popular method to study theoretically glass and liquid structures (e.g. [11, 12]). Their main advantage is to yield from the three-dimensional coordinates calculated for all atoms a variety of structural information that can often be checked against experimental data. In addition, they also provide information that escape experimental determinations and may thus point to the existence of unknown structural features.

Since they deal with the instantaneous state of a system, MD simulations rest on the Lagrangian function $L(r, \dot{r})$ of coordinates r and their time derivatives $\dot{r}$ as defined in terms of kinetic (K) and potential (U_p) energies

$$L = K - U_p \quad (12)$$

and on the Lagrangian equations of motion

$$\frac{d(\partial L / \partial \dot{r})}{dt} - \left(\frac{\partial L}{\partial r} \right) = 0. \quad (13)$$

This leads to

$$m(i)\ddot{r} = f(i), \quad (14)$$

where $m(i)$ is the mass of atom i and

$$f(i) = \nabla_{r(i)} L = \nabla_{r(i)} U_p, \quad (15)$$

where $f(i)$ is the force exerted on atom i .

If the coordinates of all atoms are known at time t_0 , all the forces exerted and the resulting velocities are calculated with Eq. (15) and then Eq. (14). All the velocities and coordinates after a time step of Δt are updated by the time integration of the equations of motion (14).

When MD methods are applied to glass or disordered systems, several important points should be noted:

- 1) As the proper choice of the interaction potential model is extremely important, a model with complex interaction potentials may be required if any dynamic structure or property is to be calculated after along with the static structure.
- 2) The particular starting configuration is not important as long as equilibration time steps are numerous enough at high temperature. Almost the same structural information should be obtained from different initial configurations. If not, the calculated results are unreliable.

Advanced techniques may be used to calculate structure and properties more efficiently. To omit unimportant contributions to the dynamics, one can, for example, keep constant bond lengths such as O—H during the MD calculation. As an alternative to this *dynamic constraint* method, one can use nonequilibrium MD, which is especially efficient to calculate transport properties such as viscosity. Unlike with conventional MD, a continual friction force can be imposed on the system and its response be monitored.

5 Modeling: Simulation Techniques and Examples

5.1 Overall Glass Structure

In atomistic simulations the positional correlation of atoms is easily investigated within a radius of half of simulation cell size (~ 25 Å). The most widely derived results are the PDF, the RDF, or total correlation function, $T(r)$, which can be readily compared with those obtained in diffraction studies.

In simulations, the PDF and the RDF are derived as follows. The single and pair (two-body) probability density $P_N^{(1)}$, $P_N^{(2)}$ are defined as

$$P_N^{(1)}(r) = \langle \sum_i \delta(r - r_i) \rangle \quad (16)$$

$$P_N^{(2)}(r, r') = \langle \sum_i \sum_{j(j \neq i)} \delta(r - r_i) \delta(r' - r_j) \rangle, \quad (17)$$

where N is again the number of atoms and r_i is the coordinate of atom i .

The value of $P_N^{(1)}(r)$ in homogeneous system turns out to be the number density ρ , which is defined as N/V , where V is the volume.

Moreover, $P_N^{(2)}(r)$ is expressed in terms of the PDF, $g(r, r')$, and number density ρ as:

$$P_N^{(2)}(r, r') = \rho^2 g(r, r'). \quad (18)$$

As to the RDF, $J(r)$, it is defined as the number of atoms between r and $r + dr$ from the center of an arbitrary origin atom:

$$J(r) = 4\pi r^2 g(r, r'). \quad (19)$$

An alternative function called total distribution function, $T(r)$, is calculated as:

$$T(r) = 4\pi \rho r g(r, r'). \quad (20)$$

The information directly obtained from diffraction experiments is the intensity $I(Q)$, which is related to $J(r)$ by

$$J(r) = 1 + \left\{ \frac{1}{(2\pi^2 \rho)} \right\} \int Q I(Q) \sin(Qr) dQ. \quad (21)$$

Finally, the frequently used structure factor, $S(Q)$, is the Fourier transform of the number density ρ_Q first calculated in atomistic simulation:

$$\rho_Q = \sum_i \exp(-iQ r_i). \quad (22)$$

Then, $S(Q)$ is calculated from ρ_Q :

$$S(Q) = \langle \rho_Q \rho_{-Q} \rangle. \quad (23)$$

It is quite important to reproduce the experimental $J(r)$ in the real space domain or $I(Q)$ in the wave-number domain to validate the calculated three-dimensional structure.

Depending on the atoms considered, X-ray and neutron diffraction experiments can yield different profiles so that both kinds of profiles should be calculated and compared with the relevant data as done in Figures 4 and 5 for MD-simulated B_2O_3 glass [6]. Once the total correlation and interference functions have been validated, more detailed analysis based on PDF functions can be performed, as shown in Figure 6, and important insight into structural order be obtained. Although the experimental peak positions are reproduced reasonably well by the calculated $T(r)$ and $Q I(Q)$, there are some discrepancies for the peak values. The position and width of the first peak represent the average length and the length distribution of B—O bonds, respectively. The second peak position and peak curve are mostly affected bond angles of O—B—O and B—O—B and size distributions. As indicated by a detailed analysis of the data, most of the discrepancy is due to a simulated fraction of only 30–50% for the so-called boroxol B_3O_6 rings (cf. Chapter 7.6) compared to the 60–80% range of the experimental values [13].

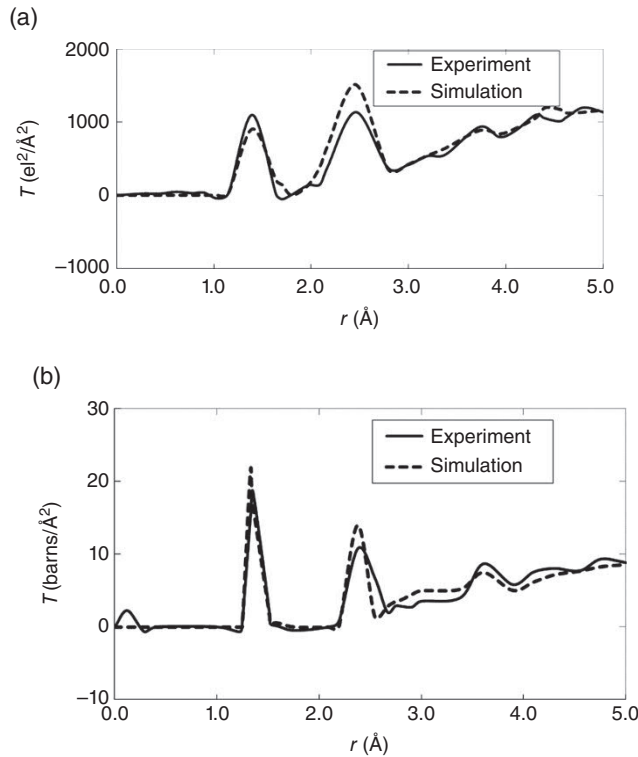


Figure 4 Comparisons between the experimental [13] and simulated [6] X-ray (a) and neutron (b) total correlation functions of B_2O_3 glass.

5.2 Short-range Order

Of particular interest for characterizing short-range order are CN. In atomistic simulation, this parameter is well defined as the number of atoms falling within a given distance from an arbitrary atom. For each atomic pair this cutoff radius is typically estimated either from the corresponding bond lengths in crystal structures or from the position of minimum between the first and second peaks of the pair-distribution function. Alternatively, the CN can be estimated experimentally from the height of the first peak observed in the X-ray diffraction or neutron diffraction spectra or from the chemical and isomer shifts in NMR or Mössbauer spectra, respectively. In MD studies the oxygen CN of network-forming cations (Si, B, P, Ge, etc.) are generally calculated to be within 5% of the experimental data even for the changes with varying pressure or concentration of network-modifier alkali or alkaline earth cations. Such coordination changes from 3 to 4 for B atoms in borate glasses and from 4 to 6 for Si and Ge in silicate and germanate glasses have been well documented in this way (e.g. [12]).

On the other hand, the oxygen CN is not well defined for intermediate network-forming cation (Al, Fe, Zr, etc.) or network-modifier cations when the distance

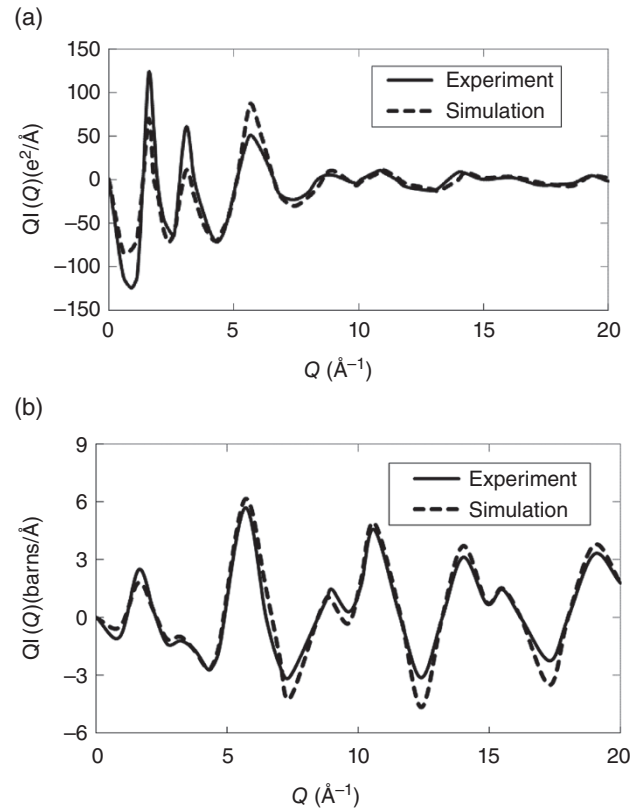


Figure 5 Comparisons between the experimental [13] and simulated [6] X-ray (a) and neutron (b) interference functions of B_2O_3 glass.

distribution between cation and oxygen atom is broad. A slight change in the definition of cutoff radius then translates in a large change in CN. In MD simulations on sodium aluminosilicate glasses, the switch of Al from a network-forming to a network-modifying role has nonetheless been evidenced by a CN increase from six in crystal to four and five in glass (e.g. [14]) whereas the existence of fivefold coordinated aluminum and threefold coordinated oxygens has also been evidenced [15].

In silicate glasses another fundamental feature to describe variations of structure and properties is the “ Q_n distribution,” where the subscript n indicates the number of bridging oxygen (BO) in an SiO_4 tetrahedra (Chapter 2.3). In MD simulations it is easy to identify nonbridging oxygens (NBO) on the basis of the cutoff radius. The calculated Q_n distributions for sodium-silicate glasses have been compared with that determined by MAS-NMR experiments [16]. The MD calculations reproduce the experiments reasonably, although the extremely rapid quenching rates prevailing in the MD simulation may broaden the distribution, which does depend on actual T, P conditions. The analysis of Q_n is also important for phosphate glasses, because Q_n

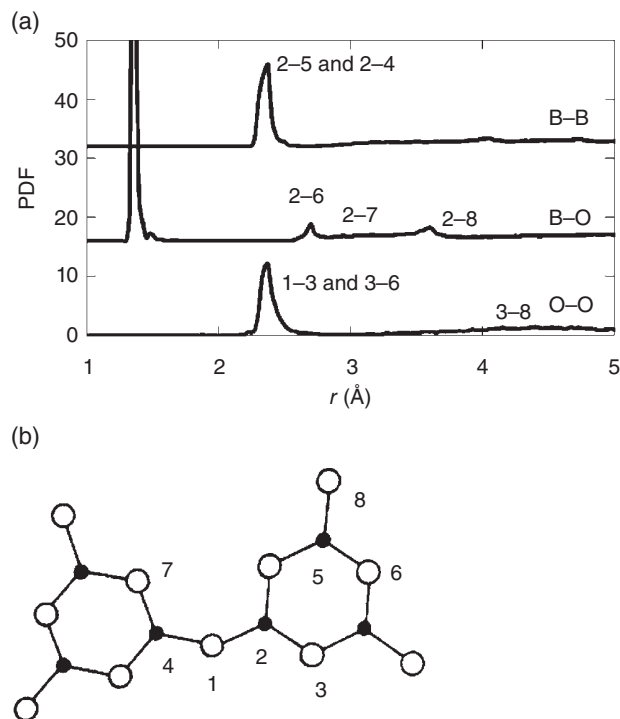


Figure 6 PDF functions in simulated B_2O_3 glass and their structural assignments [6]. The peaks labeled in (a) refer to the specific distances indicated in the elementary structural units (b).

distribution reflects their polymer-like structure that results from the existence of doubly bonded oxygen atoms. In the case of phosphate glass not many MD studies have been published and more validated potential models need to be developed. Recent MD calculations on iron phosphate glasses have demonstrated that the network connectivity is indeed dominated by the expected Q_n [11].

The third useful information on short-range order is the “bond angle distribution” (BAD), because the nature of the existing polyhedral units can be ascertained from oxygen–cation–oxygen angles. For SiO_2 and silicate glass, the simulated peak position is, for instance, found near 109.47° in O–Si–O angle distributions, which of course reflects the presence of Si within SiO_4 tetrahedra. Likewise, the peak of O–B–O angles in B_2O_3 lies around 120° , in harmony with the formation of BO_3 triangles (Figure 7). As for the B–O–B distribution, a significant amount of angles with 120° reveals the presence of boroxol rings (Figure 7) because, without boroxol rings, the B–O–B distribution should be around 129° as observed in B_2O_3 crystal [6]. In this respect, the interest of MD simulations stems from the fact that there is no direct method for determining the BAD experimentally – just a possibility to estimate roughly average values from X-ray or neutron diffraction data. These simulated cation–oxygen–cation BADs are specially valuable to probe

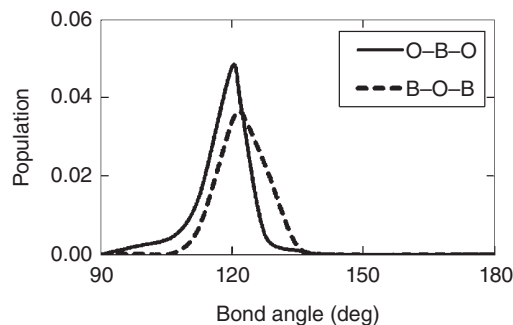


Figure 7 Bond angle distribution in simulated B_2O_3 glass.

local structural changes with either temperature or pressure in single-component glasses such as SiO_2 , B_2O_3 , P_2O_5 , or GeO_2 .

The fourth information of interest is the “torsion angle distribution” (TAD), to which particular attention is paid for polymers whose structure and properties are significantly affected by the twisted arrangement of side chains. Again, B_2O_3 glass illustrates the relevance of this distribution to inorganic glasses because of the steric problem raised by the interconnection of BO_3 units and boroxol B_3O_6 rings (Figure 8). In this case, the calculated TAD suggests different connecting geometries between BO_3 – BO_3 linkages and B_3O_6 – B_3O_6 units: the former are preferentially oriented in a perpendicular direction, which means that connected BO_3 units do not lie in the same plane, whereas the latter are oriented in the same direction, which means that B_3O_6 units do lie in the same plane [6]. For SiO_2 glass, no such distinction is of course found, but MD simulations do suggest that a torsional transformation takes place between neighboring SiO_4 tetrahedra at elevated temperature, in analogy with the structural changes associated with the α – β transition in cristobalite [17]. In addition, it has been suggested that the abrupt rotation of Si–O–Si equivalent to torsion movement between two SiO_4 tetrahedra is the cause of anomalous thermomechanical properties in silica glass [17].

5.3 Medium-range Order

Medium-range order is difficult to study either experimentally or through numerical simulations. The size distribution of rings made up of cations and oxygen atoms is in particular an important parameter when investigating geometrical features in the 5–15 Å range. Usually a ring is characterized by the number of its network-forming cations, which can be derived from the calculated atomic coordinates as shown in Figure 9 for simulated B_2O_3 and SiO_2 glasses. Compared with cristobalite, tridymite, and quartz, whose ring sizes are 6, 6, and 6 and 8, respectively, simulated SiO_2 glass shows a broad distribution around 6.

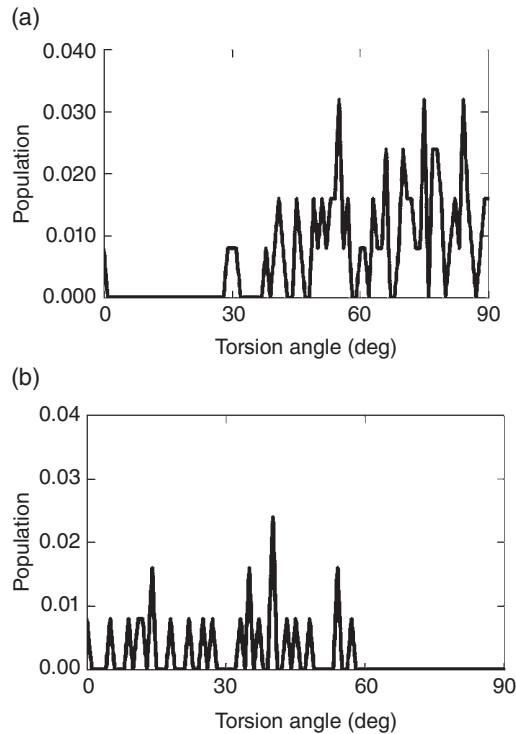


Figure 8 Torsion angle distribution in simulated B_2O_3 glass between BO_3 and BO_3 units (a) and between B_3O_6 and B_3O_6 units (b) [6]. Data sampled at 0 K to prevent peaks from being blurred by atomic vibrations.

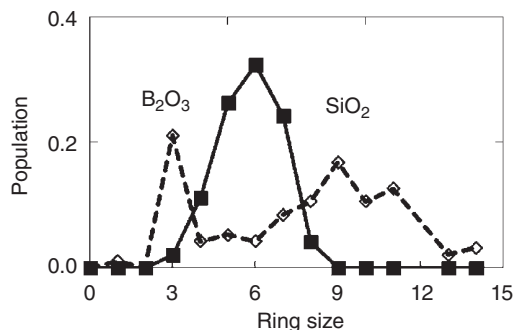


Figure 9 Ring size distribution in simulated B_2O_3 and SiO_2 glasses [11]. Data sampled at 0 K.

It has been speculated that the existence of sizes of odd-numbered rings are characteristic of disordered structures and might impede glass crystallization, because five-fold rotational symmetry does not exist in crystals where four-, six-, and eight-membered rings are primarily observed. In B_2O_3 glass, which is extremely reluctant to crystallize, the existence of B_3O_6 units indeed causes the presence of a peak at 3 in the ring statistics.

Of more general relevance is the vibrational density of states (VDOS). One can calculate it by solving the eigenvalue problem once the curvature of the energy surface

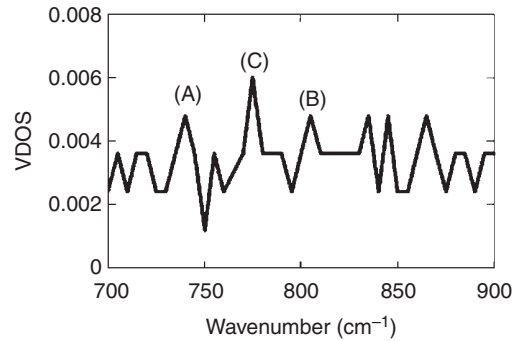


Figure 10 Vibrational density of states in simulated B_2O_3 glass [6]. See text for the assignments of the peaks labeled A, B, and C.

around the stable configuration is obtained. The VDOS for simulated B_2O_3 glass is shown in Figure 10, where the peaks labeled A, B, and C represent the vibrations associated with independent BO_3 units observed in crystalline B_2O_3 , where B_3O_6 units are absent, the breathing mode of B_3O_6 units observed in the crystal of metaboric acid comprised of B_3O_6 unit, and the vibrations of $B_3O_6 + n$ units with several BO_4 tetrahedra comprised in rings [6], respectively. The VDOS can thus provide important structural information in terms of cooperative motion of structural units.

There is another geometrical method relying on the so-called “Voronoi diagram” (e.g. [18]). It is largely employed for monatomic system for which partitioning three-dimensional space is simple and easy when the calculated atomic coordinates obtained by atomistic simulations are used to delineate the portion of space assigned to every atom. These “Voronoi polyhedra” are then characterized by their numbers of faces and corners whose distributions change as positional relationships vary in the glass structure. The other geometrical method is called the analysis of “bond orientational order.” The order parameter that is rotationally invariant can be calculated with spherical harmonic functions. This order parameter has been used to investigate a local icosahedral order chiefly for monatomic system, because its value can discriminate geometrical differences between FCC, HCP, icosahedral, and BCC clusters (e.g. [18]).

In summary, atomistic simulations provide a key to explaining the concept of “modified random network theory [10]” in alkaline silicate glass [10] or the existence of “super-structural units [19]” in B_2O_3 glass [6]. However, new analytical methods are required to understand medium-range order in more detail.

5.4 Structure-related Properties

Important thermodynamic properties can be calculated once numerical simulations have yielded atomic

configurations and velocities. The pressure is, for example, calculated from

$$P_{ij} = \left(\frac{N}{V}\right)kT - \frac{1}{(3V)} \left\langle \sum_i \sum_{j(i \neq j)} f_{ij} r_{ij} \right\rangle, \quad (24)$$

where the bracket indicates an equilibrium time average and N , V , T , f_{ij} , and r_{ij} are as usual the number of atoms, cell volume, temperature, and pair force and distance between atoms i and j , respectively.

The internal energy (E_{int}) is

$$E_{\text{int}} = \left(\frac{3}{2}\right)kT + \left\langle \sum_i \sum_{j(i \neq j)} f_{ij} r_{ij} \right\rangle, \quad (25)$$

and the molar heat capacity at constant volume (C_v):

$$C_v = \left(\frac{\partial E_{\text{int}}}{\partial T}\right)_V. \quad (26)$$

Alternatively, one can derive C_v from the potential energy fluctuations through

$$\langle U_p^2 \rangle - \langle U_p \rangle^2 = \left(\frac{2}{3}\right)Nk^2T^2 \left(\frac{1 - (3/2)k}{C_v}\right) \quad (27)$$

and two other interesting properties are the thermal expansion coefficient, (α_p)

$$\alpha_p = \left(\frac{1}{V}\right) \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{1}{T}\right) \left\{ 1 - \left(\frac{1}{V}\right) \left(\frac{\partial H}{\partial p}\right)_T \right\}, \quad (28)$$

where H is enthalpy, and the thermal pressure coefficient (β_V):

$$\beta_V = \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{1}{T}\right) \left\{ \left(\frac{\partial E_{\text{int}}}{\partial V}\right)_T + P \right\}. \quad (29)$$

After a model of atomistic simulation is validated so that it can reproduce static structure of glass, it can be applied to investigate transport and dynamical properties such as diffusion constants, viscosity, or the Van Hove correlation function (Chapter 4.6).

5.5 Experimental and Computational Complementarity

The static arrangement of structural units for B_2O_3 glass and the dynamical arrangement of structural units for SiO_2 glass represent new insights on glass structure provided by MD simulations, in these cases, by the TAD, which escape any experimental determinations. These two examples thus illustrate the complementary nature of numerical simulations and experimental studies of glass structure. When the history of structural studies on glass is looked back on, it is clear that both diffraction and spectroscopic studies have made fundamental

contributions to the construction of structural models. The RDF or the PDF can indeed be readily calculated from the Fourier transform of experimental X-ray, neutron, or electron diffraction data (Chapter 2.2). Because this type of information represents averaged one-dimensional structural data, however, there is always some arbitrariness when reconstructing the actual three-dimensional configuration in which one is interested.

Other probes such as IR, Raman, or NMR spectroscopies can provide information only on short-range order in glass structure. In contrast, atomistic simulations do provide realistic three-dimensional configuration directly as long as an appropriate atomistic model is employed. One could confidently argue that a structural model of glass is reliable when the model matches the results of both experiments and atomistic simulations. In summary, the relation between atomistic simulation and experiment is complementary because both methodologies provide insights on different aspects of glass structure. Atomistic simulations nonetheless possess two other advantages over experimental methods. The first is that they can determine three-dimensional configurations from short- to medium-range order extending up to the size of cell length (10–100 nm). The second is that a very broad range of atomistic simulations become possible as soon as an appropriate simulation model is established. For example, it is easy to change external conditions such as temperature, pressure, or other external forces to investigate their effects on structure. And physical and chemical properties can be readily derived from the potential-energy and structural models with standard statistical mechanical methods.

6 Perspectives

Development of both faster computing processors and efficient simulation algorithms have expanded the range of atomistic simulations and narrowed down their discrepancies with experiments. Simulations would nonetheless benefit from improved accuracy. As becoming more common, the best way to achieve this goal is to perform first-principles MD calculation from beginning to end. Although such calculations made with standard quantum mechanical codes remain difficult when dealing with a large number of atoms, progress should result from the use of the so-called order- N and linear scaling methods, which have developed vigorously during the past decade. For oxide glasses, recent codes such as SIESTA or CONQUEST now have the potential ability to handle systems of around one thousand atoms with a supercomputer whereas calculations for systems ten times bigger should

become feasible in the next decade. Alternatively, better classical potentials can be derived from the energy data yielded by *ab-initio* methods as well illustrated by the Tuneyuki and BKS potentials used for silica glass that were based on the simple Buckingham function [4]. Whereas parameter fitting of these potential models was handmade, automatic fitting by machine learning methods is becoming popular since a huge number of data can be sampled on potential energy surfaces yielded by first-principles calculations to derive better interatomic potentials. And even if the simulation remains based on classical mechanics, the shell, polarizable, charge-equilibrium, and other models will be more widely used to reproduce better structures and properties [4].

The two other main limitations of numerical simulations currently concern the space- and timescales considered. To cope with them, combinations of two different techniques may be used as already described in Section 3 for RMC methods. Besides, MC algorithms can be integrated into MD calculations to speed up simulation of too slow structural relaxation as is the case for the formation of boroxol rings in B_2O_3 [11]. Of more general use, however, is a combination of classical and first-principles MD simulations [20] whereby the former yield a preliminary structure that is subsequently optimized in the latter before spectroscopic or other properties are finally derived from the first-principles simulations.

The “coarse-graining” methods are also promising as multi-scale simulation procedures. By lumping groups of atoms into larger entities referred to as particles, which interact according to newly parametrized effective interaction potentials, they have been successfully used for polymers to describe slow dynamic modes and to investigate the cooperative motions and fluctuations observed in the intermediate- and long-range regions. For oxide glasses, however, their application is hampered by the difficulty of assigning appropriate structural fragments to coarse-grained units.

Finally, it is important for glass scientists to share their know-how on simulation techniques and interatomic potentials. One of such activities takes place in the TC-3 Technical committee of the International Commission on Glass (ICG) where round-robin tests are made to compare experimental data and calculated results on standard glass samples. Such an activity will provide useful information to other glass scientists on agreement and discrepancy between experiments and atomic simulations. Another activity is conducted in TC-27 whose members discuss future directions of atomistic simulations, promote standardization of atomistic techniques, and provide information on these techniques to the glass community (e.g. [21]). In addition, ICG has published an educational

textbook, which includes one chapter on atomistic simulations [22].

In a near future, we strongly expect that any macroscopic property will be explained in terms of microscopic structure by atomistic and first-principles simulations. In addition, computational design of glass materials will advance rapidly in good harmony with experimental studies.

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2.9

First-principles Simulations of Glass-formers

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1 Introduction

In their early days, i.e. in 1940–1950, computer simulations were mainly done to address questions in statistical physics, such as the properties of hard-sphere systems or the dynamics of simple crystals [1]. When a few decades later computers became more powerful and more accessible, it became possible to study the properties of real materials. For this, researchers used an approach that today is referred to as classical molecular dynamics (MD), i.e. the interactions between the particles that constitute the material are described by an effective potential with a form chosen in a rather ad hoc manner, e.g. Lennard-Jones. The parameters of the potential (e.g. the depth and the position of the well in the Lennard-Jones potential) are selected such that the density, the melting temperature for a crystal, or other macroscopic properties of the simulated system matches experimental data. Once these interactions are known, one solves numerically Newton's equations of motion and hence obtains the trajectories of all the particles (Chapter 2.8, [1]). From these trajectories, one then can determine physical properties of the system such as the radial distribution function, diffusion coefficients, or elastic constants.

Although simulation studies with effective potentials are very valuable to gain qualitative insight into the properties of liquids and solids, they usually do not allow to obtain a good quantitative description. The reason for this failure is that most properties depend in a quite sensitive manner on the potential that describes the interactions between the constituting particles of the material. Since normally these interactions depend not only on the type of atoms considered but also on the microscopic

environment of the particles (e.g. the bond strength between an oxygen and a silicon will change if a hydrogen is approached to this pair), it is basically impossible to come up with a simple potential-energy expression that could describe faithfully all these different environments. This problem is particularly pronounced for glasses where, in contrast to crystals, each atomic species has multiple local environments. At present, the only method that can address this problem in a systematic manner is the *ab initio* formalism (also called first-principles). In this approach one does not rely on a fixed functional form for the interaction potential, but uses instead the electronic degrees of freedom of all atoms to compute the forces acting on them in the system. Once these forces are known, one solves Newton's equation of motion to determine the trajectory of the particles and, subsequently, the properties of the system. Thus *a priori* the only input needed for these simulations are the species of the particles, a feature that has allowed *ab initio* simulations to become a highly attractive method to gain a detailed understanding of the properties of glass-forming liquids and glasses.

The goal of this review is to give a brief introduction to the method, discuss its advantages but also its problems, and then to present some specific examples showing that this type of simulation is indeed very useful to improve our understanding of glasses at the microscopic scale. We will first focus on structural properties in view of the major problems caused by atomic disorder, especially in complex glasses. Vibrational properties will then be examined as the heat capacity, thermal conductivity, or transparency directly or indirectly depends on them. Because solid-state nuclear magnetic resonance (NMR) yields detailed insights into the local structure of materials (Chapters 2.2 and 2.4), especially when long-range symmetry is lacking, we will conclude this chapter with a brief description of the calculation of NMR spectra.

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2 Ab Initio Simulations

2.1 General Principles

In the ab initio approach, the forces on the atoms are obtained from the electronic degrees of freedom of the system as determined from the Schrödinger equation,

$$\mathcal{H}_e \Psi = E \Psi, \quad (1)$$

where the (complex) many-electron wavefunction $\Psi(\{\mathbf{r}_i\}; \{\mathbf{R}_J\})$ depends on the positions of the n electrons, $\{\mathbf{r}_i\}$, as well as the positions of the N nuclei, $\{\mathbf{R}_J\}$ [2], E is the energy of the electronic degrees of freedom, and the operator $\mathcal{H}_e$ is given by

$$\mathcal{H}_e = - \sum_{i=1}^n \frac{1}{2} \nabla_i^2 + \sum_{\substack{i,j=1 \\ j < i}}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^n \sum_{I=1}^N \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}, \quad (2)$$

with Z_I the charge of ion I . This equation is written in atomic units, i.e. Planck's constant, the electronic charge and mass are set to unity, and the Laplacian ∇^2 is given by $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. In Eq. (1), only the electronic degrees of freedom are treated quantum mechanically whereas those of the nuclei are not. This approximation, often called “Born–Oppenheimer” or “adiabatic,” is quite accurate since the mass of the electron is almost 2000 times smaller than the one of the lightest nucleus, i.e. hydrogen. Hence, the degrees of freedom of the electrons are basically decoupled from those of the nuclei, i.e. the heavy nuclei move more slowly than the light electrons which thus adapt instantaneously to the changes of the nuclear positions. As a consequence, one assumes for the electronic structure calculations that the nuclei are clamped at fixed positions and that hence the electronic wavefunction Ψ depends on $\{\mathbf{R}_J\}$ only parametrically [2].

To reduce the computational complexity, even further one considers only the ground-state solution of Eq. (1), Ψ_0 , i.e. the electronic state with the lowest energy, which is in fact the only one that matters even for melts at high temperatures. The interaction potential between the nuclei is then given by $\Phi(\{\mathbf{R}_J\}) = \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \sum_{I,J=1, I < J}^N \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$ and the force on particle I is given by $F_I = -\nabla_I \Phi(\{\mathbf{R}_J\})$ [2].

Finding the wavefunction Ψ_0 that is the solution of the Schrödinger equation (1) is a formidable task and there are two main approaches to solve it. The first one is a wavefunction-based method, often known as the quantum-chemistry approach, which starts from the Hartree–Fock method. In a first-order approximation, it factorizes the many-body electronic wavefunction into

one-particle wavefunctions whose ground states are then searched numerically. Although at present the solution is found in a reasonable amount of time for several tens of atoms, new methods have been proposed in this field with very promising results for systems ten times bigger. The second method, which will now be described in some detail, is the density functional theory (DFT).

2.2 Density Functional Theory

The DFT formalism exploits certain ground-state properties of many-electron systems in an external field, thus in our case the Coulomb field of the nuclei. Following up ideas proposed by Thomas and Fermi in the 1930s, it has been rigorously established by Hohenberg, Kohn, and Sham in the early 1960s [2], who showed that the total energy of the system is a functional of the electronic density. DFT gets rid of the many-body wavefunction, which depends on $3n$ electronic spatial coordinates, and replaces it by the simpler electronic density $\rho(\mathbf{r})$ that only depends on three spatial coordinates:

$$\rho(\mathbf{r}) = \int \dots \int d\mathbf{r}_2 \dots d\mathbf{r}_n \Psi_0^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n) \Psi_0(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n). \quad (3)$$

Kohn and Sham [3] showed that this density can be written as a sum of the density of noninteracting particles, $\rho(\mathbf{r}) = \sum_i^n |\phi_i(\mathbf{r})|^2$, where ϕ_i are the fictitious one-particle Kohn–Sham (KS) orbitals, and thus the ground-state density $\rho_0(r)$ is given by the sum of the ground states of these particles. Hence, the total energy of the system can be expressed as

$$E_{\text{KS}}[\rho] = T[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) \left[\frac{1}{2} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right] + E_{\text{xc}}[\rho], \quad (4)$$

where $T[\rho]$ is the kinetic energy of a system of n noninteracting electrons having the density ρ ,

$T = -\frac{1}{2} \sum_{i=1}^n \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$, and the second term is the Coulomb interactions between electron–electron and electron–nuclei. The third term is the so-called exchange and correlation energy which accounts for all quantum many-body effects due to the Pauli exclusion principle which correlates electrons. Since this term cannot be evaluated exactly, approximations have to be made. Even though $E_{\text{xc}}[\rho]$ is usually substantially smaller than the two other terms, the manner it is approximated may become crucial for chemically complex systems [2].

The simplest one, proposed originally by Kohn and Sham [3], relies on the assumption that at each point the exchange-correlation energy density corresponds to that of a homogeneous gas of electrons. This approximation is called the “local density approximation” (LDA) and is given by:

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}^{LDA}[\rho(\mathbf{r})]. \quad (5)$$

Even for such a simple model system, the expression of the correlation energy has to be calculated numerically with Monte-Carlo methods. A more advanced approximation, the so-called “generalized gradient approximation” or GGA, is based on a more complex operator making use of the density gradient of m th order:

$$E_{xc}^{GGA}[\rho(\mathbf{r})] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}^{GGA}[\rho(\mathbf{r}); \nabla^m \rho(\mathbf{r})]. \quad (6)$$

However, this higher approximation does not necessarily give more reliable results so that it is a priori not clear which exchange-correlation functional should be used [2]. Despite this problem one can say that the KS approach and reasonable (simple) approximations for the exchange-correlation term have opened the door to the calculations of the electronic structure for many-atom systems relevant to the study of real materials.

Although expressing the full quantum mechanical problem in the language of DFT leads to a significant reduction of the computational effort for calculating the forces on the nuclei, in practice this task is still extremely demanding when dealing with more than a few tens of atoms. Therefore, one usually makes the further approximation that all the core electrons of an atom are lumped together so that their effect is replaced by an effective potential, the so-called “pseudo-potential,” for the remaining valence electrons which are described by a pseudo-wavefunction [2]. The physical motivation for this approximation is that the chemical bonds between two atoms are usually related to the outer valence electrons and thus depend only weakly on the inner core electrons.

2.3 Computational Limitations

So far, we have discussed how DFT allows one to obtain the forces between the nuclei due to their surrounding electrons. These forces can now be used to solve the equations of motion for the nuclei:

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_{KS}[\{\phi_i\}, \mathbf{R}], \quad (7)$$

where the energy $E_{KS}[\{\phi_i\}, \mathbf{R}]$ can be calculated from the KS orbitals within the KS scheme of the DFT. In the above equations the nuclei are considered as classical particles

and Eq. (7) is solved using the same methods as in classical MD (see Chapter 2.8 or [1] for details). Because of the resulting motion of the ions, the electronic structure changes and hence one has in principle to recalculate the total energy of the electronic ground state, a procedure that is computationally very costly even within the DFT approach. One possibility to avoid this problem was proposed in a seminal paper by Car and Parrinello in 1985 [4]. The idea behind this so-called Car–Parrinello molecular dynamics (CPMD) is to introduce a fictive dynamics to the electronic degrees of freedom and thus to recast the quantum mechanical problem into a classical one with the electronic wavefunctions as new effective degrees of freedom.

Although the CPMD approach allows to obtain the correct equilibrium properties of a system, the introduction of the fictive dynamics for the electronic degrees of freedom makes that the motion of the system in configuration space is not completely realistic [2]. Despite this shortcoming, CPMD simulations are still widely used to study complex systems by means of computer simulations (cf. software available at <http://www.psi-k.org/codes.shtml>). This problem can, however, be avoided with the so-called Born–Oppenheimer molecular dynamics (BOMD) in which one solves at each time step the electronic problem. This approach thus allows to give a correct dynamics but at the cost of an increased computational load. Only in the last few years the numerical algorithms have been improved to such an extent that today it is possible to simulate within BOMD several hundreds of particles [5, 6].

This brief description of the ab initio simulations should make it clear that in practice the codes for such simulations must be extremely optimized in order to keep the necessary computer time within a reasonable limit. This is why, in contrast to simulations performed with effective potentials, first-principles calculations are not made with “homemade” codes but with one of the very sophisticated and highly optimized packages that have been developed over the years. Various groups use different approaches to maintain and develop these packages, the most popular ones being CPMD, VASP, Quantum Espresso, CP2K, Siesta, CASTEP, etc. (see on <http://www.psi-k.org/codes.shtml> for a more extended list). Each of them has advantages and disadvantages regarding the scaling of computational effort with system size, accuracy, ensembles that can be simulated (microcanonical, canonical, constant pressure, etc.), quantities that can be calculated, etc., and therefore the best choice will depend on the application.

To give an idea of what can be done at present with ab initio simulations, we compare in Table 1 ab initio and classical simulations. Since the computational load for the former does depend on the system considered

Table 1 Comparison of various features of large-scale computer simulations carried out with classical and ab initio methods.

	Classical MD	Ab Initio MD
Size	1 000–500 000 atoms	100–500 atoms
Box size	~100 Å	~15–20 Å
Trajectory length	~1 ns–10 μs	~20–100 ps
Transferability	No	Yes

(owing to the different electronic structure for the atoms), we will consider the example of an oxide glass. We note that, for a given computing time, there is trade-off between the size of the system and the time span covered by the calculation. For a classical system the relevant number is basically the product of the two quantities so that doubling the system size increases the computer time by a factor of two. For ab initio simulations the situation is not that favorable since doubling of the system size usually leads to an increase of the computational load by a factor of 2^α , where α is about 3. As a consequence, system sizes are smaller and accessible timescales are shorter in ab initio than in classical simulations. Therefore, the quench rates used to cool a system from its liquid to its glass state are usually on the order of 10^{13} – 10^{15} K/s. Such rates are thus significantly larger than those of classical simulations (10^{10} – 10^{14} K/s) and of course ways higher than experimental values (10^{-2} – 10^6 K/s). Despite these huge differences, the resulting glasses are surprisingly similar since many of their properties depend only in a logarithmic way on these rates. Therefore, it does make sense to use ab initio simulations to investigate the properties of glasses on the microscopic scale.

3 Structural Properties

In this section we will present some examples to illustrate *how* ab initio simulations can help to gain a better understanding of the local structure of complex glasses. The very first ab initio MD simulations for a glass-former were carried out by Sarnthein et al. in 1995 on silica [7]. Using the Car–Parrinello approach, they generated a glass model by equilibrating for 10 ps a liquid sample with 72 atoms (!) at 3500 K and subsequently quenching it to 300 K. Despite the smallness of the system and the high quench rate (10^{15} K/s!), the resulting glass structure was surprisingly similar to that of the real material with a network of SiO_4 corner-sharing tetrahedra and a neutron structure factor compatible with the that from scattering experiments. These authors also found that their electronic density of states matched well the X-ray

photoelectron spectroscopy data although the predicted band gap of 5.6 eV underestimated the experimental value of about 9 eV, a flaw that often occurs in DFT calculations [2].

This pioneering paper was followed by further investigations in which more complex glass-formers were studied, such as alkali silicate glasses, calcium-alumino-silicates [8–11], and other glass-formers [12, 13]. These investigations allowed to obtain detailed insight into the local arrangement of the atoms, how network modifiers like Na or Ca change these arrangements, and the connections between local structure in real space with structural features as determined in neutron or X-ray scattering experiments.

As an example we will briefly discuss some results obtained for sodium borosilicate of composition 30% Na_2O –10% B_2O_3 –60% SiO_2 (in mol %), an important glass-former in which boron atoms bond to either three or four oxygen neighbors, which makes its structure rather complex, Chapter 7.6, [6]. One important quantity to characterize the structure is the partial radial distribution functions $g_{\alpha\beta}(R)$ which is directly proportional to the probability that two atoms of type α and β are found at a distance r from each other (Chapter 2.2). Thus, this function is defined as [14]

$$g_{\alpha\beta}(R) = \frac{V}{4\pi R^2 N_\alpha (N_\beta - \delta_{\alpha\beta})} \sum_{I=1}^{N_\alpha} \sum_{J=1}^{N_\beta} \langle \delta(R - |\mathbf{R}_I - \mathbf{R}_J|) \rangle, \quad (8)$$

where $\langle \cdot \rangle$ represents the thermal average, V is the volume of the simulation box, N_α is the number of particles of species α , and $\delta_{\alpha\beta}$ is the Kronecker delta.

For the boron-oxygen pair (Figure 1a), the first peak of the radial distribution function is relatively large and slightly asymmetric. By considering three- and fourfold coordinated boron atoms, $^{[3]}\text{B}$ and $^{[4]}\text{B}$, respectively, we can decompose this peak into two contributions and see that the broadening of the total peak is a consequence of the presence of these two populations, the $^{[3]}\text{B}$ –O and $^{[4]}\text{B}$ –O bonds giving rise to the smaller and larger distances, respectively. We can decompose these distributions further by considering the nature of the second nearest neighbor of the central boron atoms, i.e. whether the nearest oxygen is bridging connected to a Si or B atom, or whether it is a non-bridging oxygen. We see that for the case of the $^{[3]}\text{B}$ atoms, the nature of this second nearest neighbor species influences the B–O distance since the position of the corresponding peak depends on the species, whereas this is not the case for the length of the $^{[4]}\text{B}$ –O bonds. The presence of $^{[3]}\text{B}$ and $^{[4]}\text{B}$ units is also reflected in the OBO triplet angle distribution (shown in Figure 1b) by the presence of two peaks.

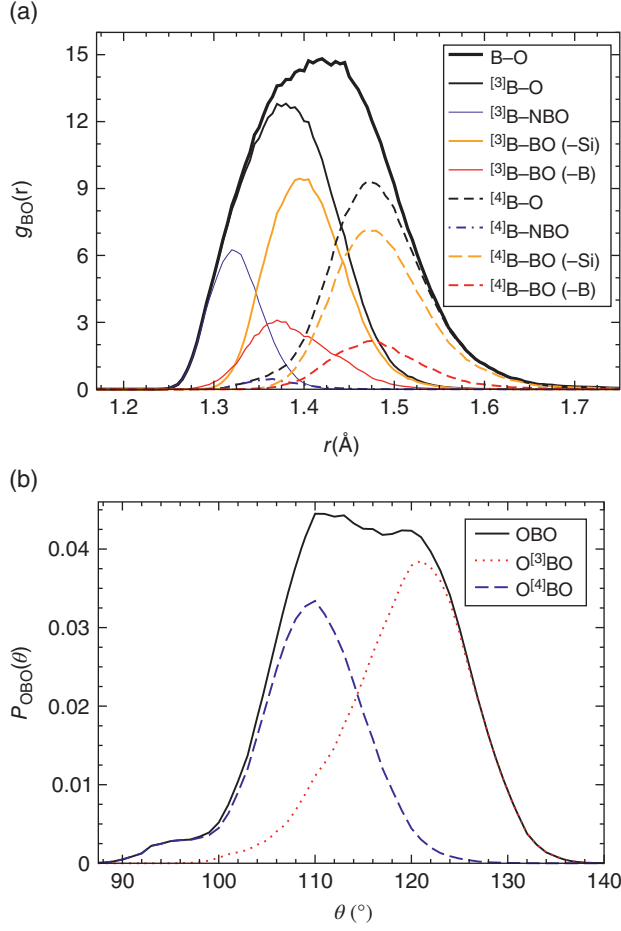


Figure 1 Contributions of the various structural units of a sodium borosilicate glass to structural features [6]. (a) Distribution of B—O distances around a given B atom as given by the first peak of the partial radial-distribution function. (b) Distribution of the angle formed by two oxygens connected to the same boron.

Although this detailed information is valuable to understand better the local structure of the glass, it is also important to connect the results from the simulation with experimental data. Even if radial distribution functions cannot be directly accessed experimentally, it is possible to measure the static structure factor, which is directly related to the weighted sum of $S_{\alpha\beta}(q)$, the space Fourier transform of $g_{\alpha\beta}(R)$ [14]. For neutron scattering, one finds, for example:

$$S_N(q) = \frac{N}{\sum_{\alpha} N_{\alpha} b_{\alpha}^2} \sum_{\alpha, \beta} b_{\alpha} b_{\beta} S_{\alpha\beta}(q). \quad (9)$$

Here, b_{α} is the neutron scattering length of particles of species α [14] and the partial static structure factors are given by

$$S_{\alpha\beta}(q) = \frac{f_{\alpha\beta}}{N} \sum_{j=1}^{N_{\alpha}} \sum_{K=1}^{N_{\beta}} \langle \exp(i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_K)) \rangle, \quad (10)$$

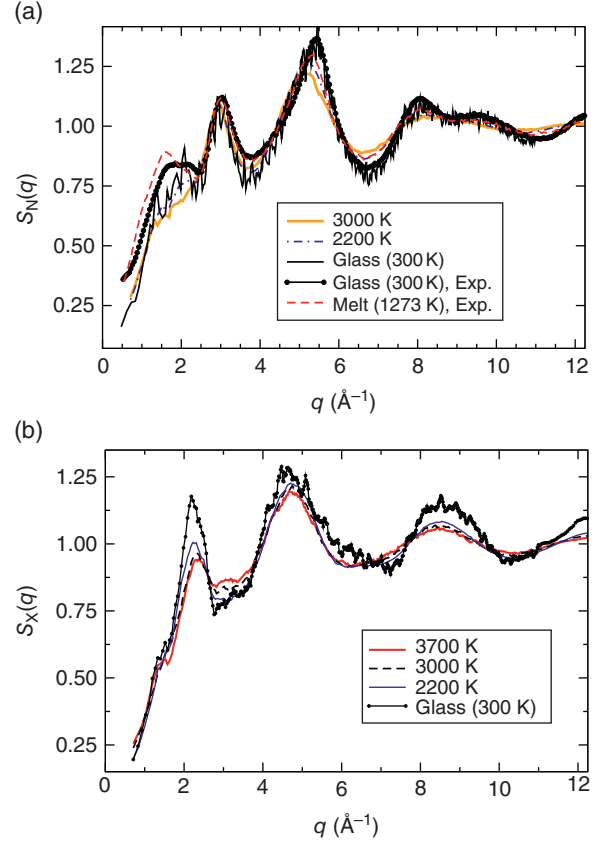


Figure 2 Neutron and X-ray structural factors (a and b panel, respectively) for a borosilicate system in the liquid and glass state. Source: From Ref. [6].

where N is the total number of atoms and $f_{\alpha\beta} = 1$ for $\alpha = \beta$ and $f_{\alpha\beta} = 1/2$ otherwise. For X-ray scattering, the relation is

$$S_X(q) = \frac{N}{\sum_{\alpha} N_{\alpha} f_{\alpha}^2(q/4\pi)} \sum_{\alpha, \beta} f_{\alpha}(q/4\pi) f_{\beta}(q/4\pi) S_{\alpha\beta}(q), \quad (11)$$

where $f_{\alpha}(s)$ is the scattering-factor function (also called form factor). Figure 2 shows that even for the same glass sample, $S_N(q)$ and $S_X(q)$ are rather different since both are a *weighted* sum of the partial structure factors, each of which has a multitude of positive and negative peaks. Hence, the resulting sum may show a peak for $S_N(q)$ that is basically absent in $S_X(q)$. Since interpretation of experimental data is further complicated by the fact that one has $k(k+1)/2$ partial structure factors in systems with k species, computer simulations can help to interpret correctly the various peaks if they do reproduce the partial structure factors in terms of peak positions and heights. As a matter of fact, the necessary accuracy is usually ensured only by ab initio simulations.

Another important situation is that of surfaces, for which experimental scattering techniques involving grazing-ray geometries are much less powerful to obtain microscopic information. Because effective potentials are usually developed for bulk systems, their reliability is not guaranteed for surfaces for which the local structure can be very different. One example are two-membered rings in SiO_2 that are present at the surface but absent in the bulk. Hence, *ab initio* simulations are to be preferred for investigating surfaces since they can deal with such heterogeneous geometries.

One interesting example of surface effects is the difference between the interatomic distance and bond-angle distributions of water molecules in the bulk and adsorbed at the surface of amorphous silica (Figure 3). Although

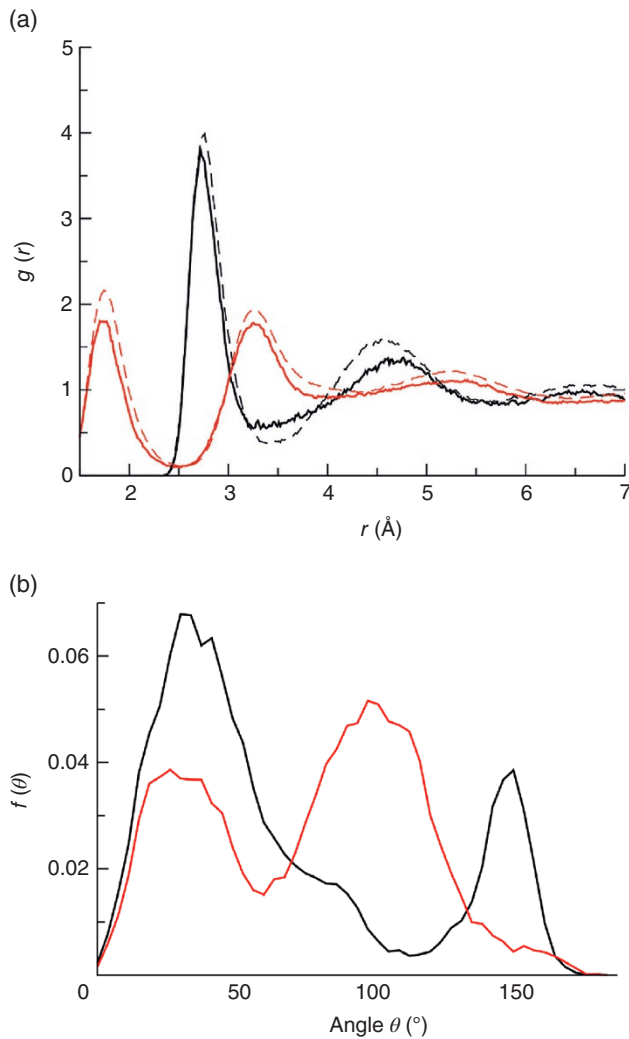


Figure 3 Structural differences between bulk (BW) and surface (SW) water in SiO_2 glass [15]. (a) Water–water radial distribution function. (b) Distribution of the angle θ between the water dipole (bisecting the HOH angle) and the surface normal.

there are no significant differences in the positions of the O—O and O—H peaks (Figure 3a), close to the surface the fluid is less structured than in the bulk as signaled by smaller peaks. Likewise, differences concerning the angle between water dipole (i.e. the bisector of the HOH angle) and the surface normal (Figure 3b) indicate a strong change of the local geometry. Only accurate interaction potentials, such as *ab initio* simulations will be able to pick up these effects.

4 Vibrational Properties

The vibrational density of states (vDOS) $g(\omega)$ is the normalized distribution function of the eigenfrequencies ω_p of the dynamical matrix of the system which is directly related to the second derivative of the potential with respect to the coordinates $\mathbf{R}_i$ and $\mathbf{R}_j$, i.e. $\partial^2 \Phi / (\partial \mathbf{R}_i \partial \mathbf{R}_j)$ for $i, j \in \{x, y, z\}$, thus

$$g(\omega) = \frac{1}{3N-3} \sum_{p=4}^{3N} \delta(\omega - \omega_p), \quad (12)$$

where $3N-3$ is the number of eigenmodes with nonzero frequency. Associated with each eigenfrequency ω_p of the dynamical matrix is an eigenvector $\mathbf{e}_p$ that gives detailed information regarding the particles that oscillate with the frequency ω_p . Studies of $\mathbf{e}_p$ have allowed to gain insight into the nature of the vibrational modes of various materials such as silica and germania glasses [12, 16–18] and more complex systems ([6, 10, 11, 19], Chapter 3.4).

The structure of a solid is related to a balance of the forces between its atoms, i.e. to the first derivative of the potential since these forces must mutually compensate to ensure a mechanically stable equilibrium. In contrast, vibrational properties are related to the curvature of the potential, i.e. to its second derivatives. As a consequence, it is quite hard to find effective potentials that reproduce correctly the experimental vDOS, even for systems as simple as pure silica [20].

The true vDOS given by Eq. (12) is not directly accessible in experiments, in which only an effective vDOS, $G(\omega) = C(\omega)g(\omega)$, can be measured. The function $C(\omega)$ describes how the modes with frequency ω are coupled to the probing radiation (photons, neutrons, etc.). For inelastic neutron-scattering experiments, this function can be derived, within approximations, from the eigenvectors $\mathbf{e}_p$ of the dynamical matrix [21].

In practice, the vibrational properties of a system can be calculated in two different ways. The first is to determine the local potential minimum of the glass structure (i.e. to quench the sample to $T = 0$ K) and then to calculate directly the dynamical matrix, for instance, by a finite-difference scheme for the forces. By diagonalizing this

matrix, one can then obtain its eigenfrequencies and eigenvectors and, hence, $g(\omega)$. The second method consists in running a simulation in which one solves Newton's equations of motion at low temperatures where the harmonic approximation is valid. If one measures the time autocorrelation function of the velocity of a particle, its time Fourier transform is directly proportional to the vDOS. This approach is from the computational point of view cheap, but it has the drawback of not giving any information on the eigenvectors, i.e. on the nature of the motion of the atoms.

The advantages of ab initio over effective pair-potential simulations are illustrated by the neutron-effective vDOS for silica (Figure 4). The effective potentials give a surprisingly good description of the structural properties of real silica [23] and also of the high-frequency vDOS where modes concern intra-tetrahedral excitations [18]. However, the vDOS calculation with the effective potential gives a broad, flat band between 200 and 600 cm^{-1} whereas the ab initio simulations show, in agreement with the experimental data, a marked peak at around 400 cm^{-1} [17].

A further technique used to get insight into the vibrational properties of glasses are measurements of dielectric properties (Chapter 3.4), which are directly related to the local polarizability of the material. Because ab initio simulations do give a good description of polarizability, they allow the high-frequency (ϵ_∞) and static dielectric constant (ϵ_0) to be accessed directly. Also called relative permittivity, the former quantity can be estimated as one third of the trace of the purely electronic dielectric tensor

$(\epsilon_\infty)_{ij} = \delta_{ij} + \frac{4\pi}{V} \frac{\partial^2 E_{\text{tot}}}{\partial \mathcal{E}_i \partial \mathcal{E}_j}$, which describes the reaction of

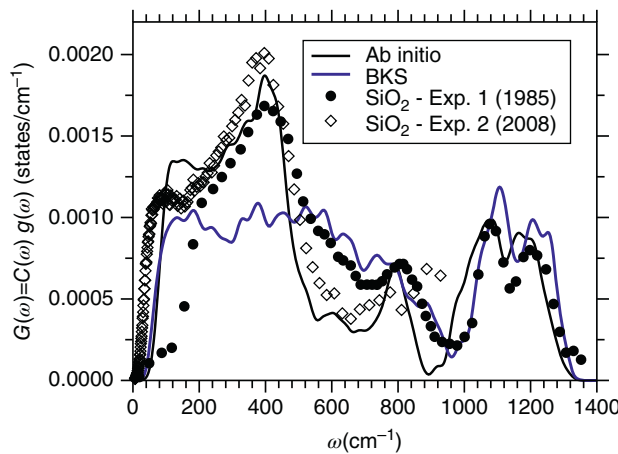


Figure 4 Effective neutron densities of states for a-SiO₂ as obtained from an ab initio simulation (solid black line) and a simulation with an effective force field (solid blue line), after [17]. Symbols: Data from two neutron scattering experiments [22]. (See electronic version for color figures).

the electrons to the presence of an external electric field if the ions were kept at fixed positions. For a glass, this tensor is basically isotropic and diagonal. The static dielectric constant ϵ_0 reflects the ionic displacement contributions to the dielectric constant and it can be expressed as [24]:

$$\epsilon_0 = \epsilon_\infty + \frac{4\pi}{3V} \sum_p \sum_j \frac{|\mathcal{F}_j^p|^2}{\omega_p}, \quad (13)$$

where p runs over all the eigenmodes, and $\mathcal{F}_j^p$ is the so-called oscillator strength which is defined as

$$\mathcal{F}_j^p = \sum_{I,k} \frac{\mathbf{e}_{I,k}(\omega_p)}{\sqrt{m_I}} Z_{I,jk}. \quad (14)$$

Here, $\mathbf{e}_{I,k}(\omega_p)$ is the part of the eigenvector $\mathbf{e}(\omega_p)$ that contains the three components of particle I , and the quantity $Z_{I,jk}$ is the Born effective charge tensor defined as:

$$Z_{I,ij} = \frac{\partial F_i^I}{e \partial \mathcal{E}_j} \quad I = 1, 2, \dots, N, \quad i, j \in \{x, y, z\}, \quad (15)$$

where e is the elementary charge, i.e. $Z_{I,ij}$ is an effective charge that connects the strength of an external electric field $\mathcal{E}$ to the force F^I on particle I .

These quantities allow to obtain immediately the real and imaginary parts of the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ [24]:

$$\epsilon_1(\omega) = \epsilon_\infty - \frac{4\pi}{3V} \sum_p \sum_j \frac{|\mathcal{F}_j^p|^2}{\omega^2 - \omega_p^2} \quad (16)$$

$$\epsilon_2(\omega) = \frac{4\pi^2}{3V} \sum_p \sum_j \frac{|\mathcal{F}_j^p|^2}{2\omega_p^2} \delta(\omega - \omega_p). \quad (17)$$

Closely related to $\epsilon(\omega)$ is the absorption spectra $\alpha(\omega)$ which is given by

$$\alpha(\omega) = 4\pi\omega n''(\omega), \quad \text{with } n''(\omega) = \sqrt{\frac{\epsilon_1^2 + \epsilon_2^2 - \epsilon_1}{2}}. \quad (18)$$

All these functions can be measured directly. On one side, they allow to test the predictive power of the simulations and, on the other, they help to interpret the various features found in the experimental spectra. For the infrared spectra of amorphous silica (Figure 5a–c), the theoretical calculation reliably predicts the position of the various peaks although their widths do not match very well the experimental data [18]. For the more complex NBS glass, a broad band is observed below 300 cm^{-1}

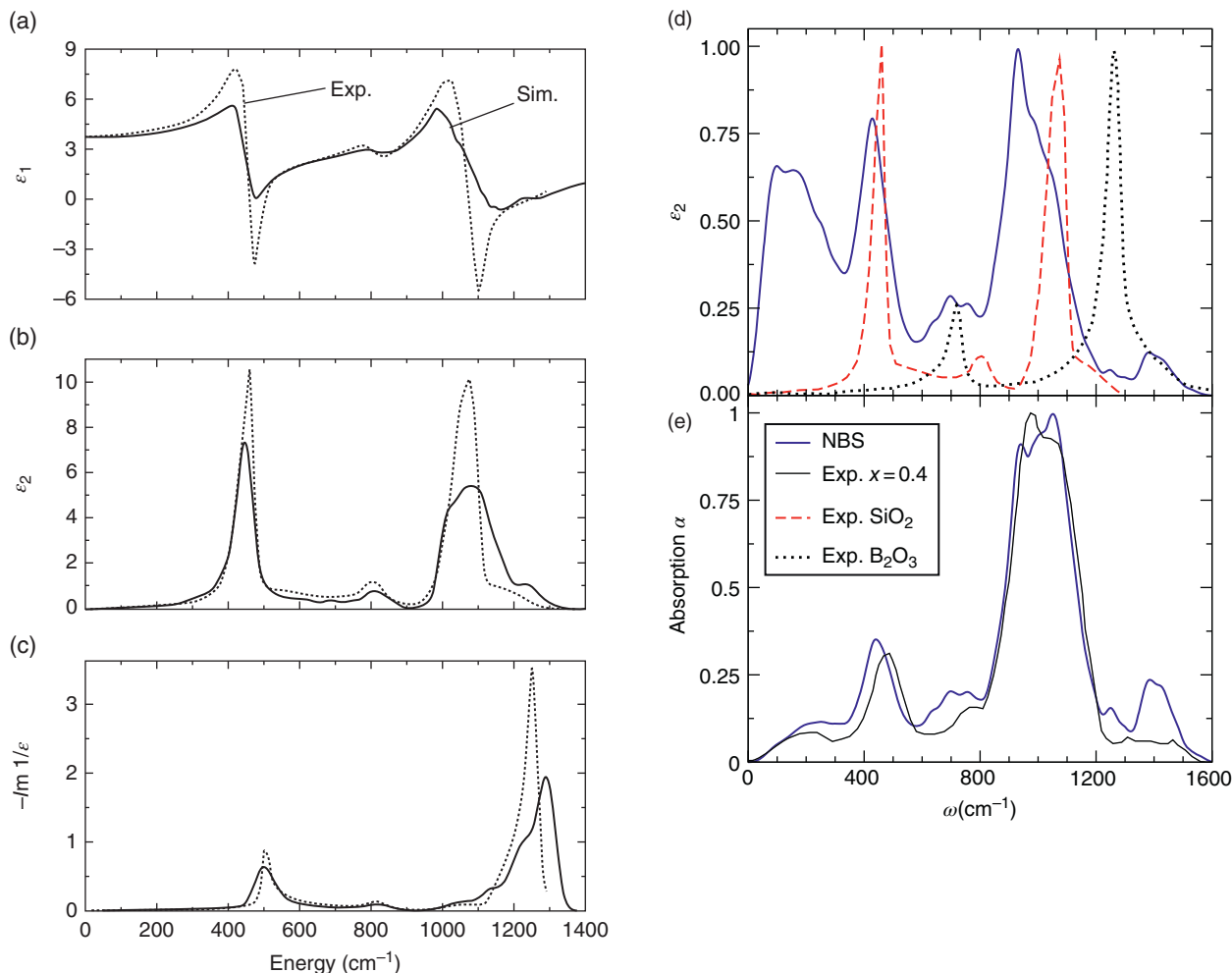


Figure 5 (a)–(c): Infrared spectra for amorphous SiO_2 as obtained from ab initio simulations (solid lines) and from experiments (dotted lines) [18]. (d) and (e): Infrared spectra for a sodium borosilicate glass as obtained from ab initio calculations and compared to experimental data for pure SiO_2 and B_2O_3 glasses, as well as for a sodium borosilicate glass with a similar composition [6].

where the vDOS is strongly dominated by the motion of Na atoms [6], which explains why the spectra of alkali-free glass-formers lack such a low-frequency band. In contrast, the narrow band found slightly above 400 cm^{-1} is also present in the spectrum of pure silica where it has been assigned to the bending and rocking motion of oxygen atoms [16]. Therefore, this peak has probably the same origin in NBS as in SiO_2 although it is somewhat broader and shifted to lower frequencies as a result of a more disordered structure.

At high frequencies one finds two bands. The first one, ranging from 850 to 1200 cm^{-1} , can be assigned to oxygen stretching modes of Si–O bonds. That this band lies at lower frequencies than for silica (sharp peak at around 1070 cm^{-1}) is consistent with earlier results showing that the presence of non-bridging oxygen atoms shifts the band to lower frequencies [19]. The second band extends between 1200 and 1600 cm^{-1} , and is due to the motions of

oxygen atoms belonging to $^{[3]}\text{B}$, in agreement with the fact that B_2O_3 , which has mainly $^{[3]}\text{B}$ units, shows a very pronounced peak in this frequency range. Regarding absorption, good agreement is again found between the spectrum of NBS and the ab initio calculations made for a closely related composition (Figure 5d and e). The main deviation is found at high frequency where a peak is absent in the experimental spectrum but present in the simulation, since the latter overestimated the concentration of $^{[3]}\text{B}$ units because of the high quenching rate [6].

Finally, we mention that DFT-based methods have also been proposed in order to compute Raman and hyper-Raman spectra for periodic solids [25, 26]. These approaches have been used to calculate the corresponding spectra for the main oxide network-formers, i.e. SiO_2 , B_2O_3 , or GeO_2 , with a good a very good agreement to experimental data [12, 13, 18].

5 Calculations of NMR Spectra

A serious problem faced by NMR experiments on disordered structures is that the observed peaks may overlap so that real-space interpretations of the spectra are not always straightforward. Theoretical calculations can thus give helpful guidance, but their difficulty is illustrated by the fact that the first NMR schemes have been proposed only 15 years ago. In the glass community, the so-called GIPAW approach proposed by Pickard and Mauri [27] is certainly the most used one, and implemented in many ab initio packages. However, the theory on how this is done is rather involved, see Ref. [28], and therefore we just illustrate the kind of results obtained with calculations of ^{29}Si Magic Angle Spinning spectra done for binary alkali and alkaline earth silicates (Figure 6).

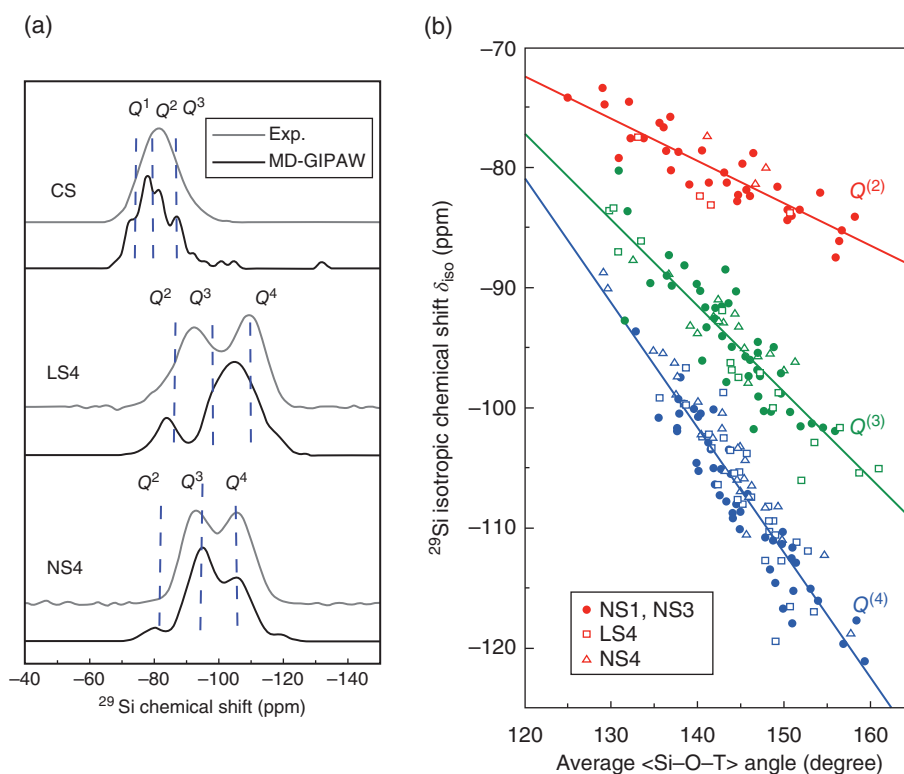
Regarding the peak positions, the agreement between the ab initio simulations and the experimental spectra is remarkably good (Figure 6a). For lithium silicates, slight discrepancies are found for the peak intensities but they are likely due to the modest size and high quenching rates of the simulated samples. In fact, one can handle this problem by determining how the concentrations of the various structural units depend on the cooling rate (or on the temperature of the liquid) and then adjusting them to the actual experimental conditions [6].

Although NMR experiments provide information on the nature of the local structure ($Q^{(n)}$ -species, connectivity of the atoms, etc.) it is difficult to extract direct information on the geometry of the local structures, such as bond angles. That ab initio simulations are also useful for this is demonstrated in Figure 6b where we show the chemical shift as a function of Si–O–T angle, where O is a first nearest neighbor of Si atom and T is the second Si atom bonded to that O. The data clearly show: (i) that there is a linear relationship between this angle and the chemical shift, (ii) that this relationship is basically independent of the composition of the glass, and (iii) that its slope depends on the $Q^{(n)}$ -species of the second Si atom.

6 Perspectives

Ab initio simulations of glasses have now become standard to determine observables of high practical relevance, but usually inaccessible to simulations with effective potentials. Despite their computational cost, they constitute a most useful tool to gain insights into microscopic properties of glasses, especially when their composition is complex, and even to develop novel types of glasses with exotic compositions. Their accuracy makes them most useful when a multitude of possible local atomic

Figure 6 Application of ab initio simulations to NMR spectroscopy [29]. (a) ^{29}Si magic angle spinning spectra of calcium metasilicate (CS), lithium tetrasilicate (LS4), and sodium tetrasilicate (NS4) glasses. (b) Dependence of the ^{29}Si isotropic chemical shifts on the Si–O–T angle calculated for different $Q^{(n)}$ species in 43 Na₂O–57 SiO₂ (NS1), 22.5 Na₂O–77.5 SiO₂ (NS3), NS4, and LS4 glasses. Solid lines: linear fits to the data.



environments coexist either in the bulk or at glass surface or when important structural heterogeneities are found at a microscopic scale. This applies, for instance, to the properties of the charged and neutral defects in amorphous silica, as their presence can strongly affect the performances of electronic and optical devices based on SiO_2 [30]. The technologically important chalcogenide glasses (Chapter 6.5) can only be simulated with force-fields accounting correctly for homopolar bonds, i.e. *ab initio* simulations. Because chalcogenides do not contain oxygen, an element that is relatively costly to deal with, they can be investigated with smaller efforts per particle and, thus, quite large systems sizes and accessible time-scales [31–33].

Other important topics are the effects of water on bulk and surface properties because the high reactivity of hydrogen induces local modification of the structure which can change the properties of the glass even at very low concentrations. The difficulty is then that fairly large systems must be investigated, which is the reason why relatively few simulations have been done on complex water-bearing glasses [9, 15]. At present, the main problem faced indeed remains the large computational effort required and hence more efficient methods are being devised to reduce the computing time. Examples are the so-called “order- N ” algorithms, with which the computational cost increases only linearly with the system size [34], or the second-generation Car–Parrinello approach [35]. Although these advances will make it possible to deal with much larger systems, including, for instance, 10^4 oxygen atoms, it is unlikely that they will allow to gain one more order of magnitude in system size. To study problems like the mechanical behavior of glasses on the mesoscale, simulations will thus have to be done with effective potentials. But even in these cases *ab initio* simulations will be very useful by providing more accurate potential parameters [36–38].

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Section III. Physics of Glass

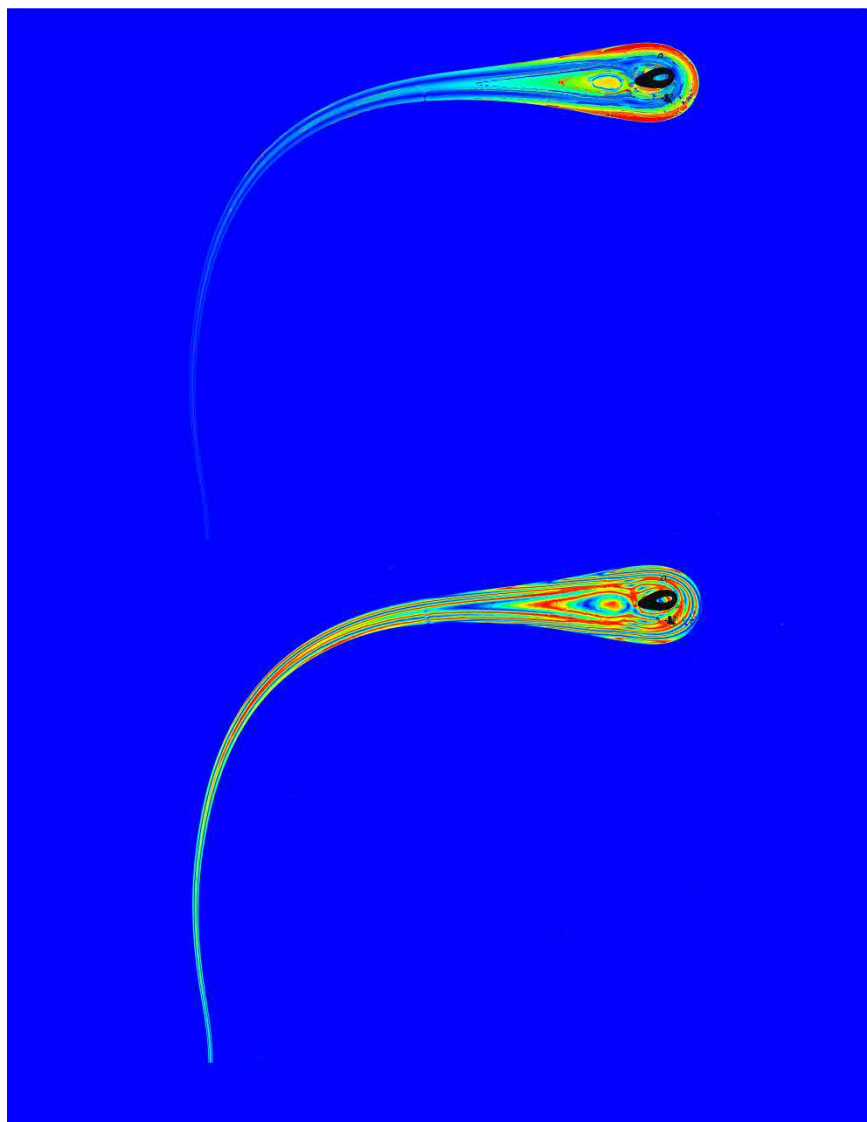


Figure 1 The influence of quench rate on the physical properties of a window glass: thermal strengthening visualized by the distribution of internal stresses in a Prince Rupert's drop (top). Determination made from an analysis of high-precision polarimetry measurements (bottom) of the strain birefringence (Strain-Matic®, Ilis GmbH, Germany). *Source:* Photo by Henning Katte of a drop prepared by Armin Lenhart, courtesy Dominique de Ligny.

In most applications glass needs to be inert with respect to its environment. A particular glass is then selected for a given use on the basis of its physical properties. The range of glasses to be dealt in both industrial and natural contexts makes it necessary to pay attention to the strong dependences of physical properties on chemical composition, whose understanding is facilitated by the structural concepts presented in Section II. Because one produces most glasses by cooling melts, however, the fundamental issues to be discussed first are why vitrifiability varies so much with composition and how the glass transition varies with the cooling rate.

In the first chapter of this section both issues are discussed by M.J. Ojovan in the light of energetic, microscopic, and structural criteria (Chapter 3.1). Owing to the nonequilibrium nature of the glass transition, its thermodynamic treatment requires new concepts. From the notions of affinity and order parameter and simple relaxation models based on calorimetric measurements, insights are derived by J.-L. Garden and H. Guillou on the entropy irreversibly created at the glass transition and on processes such as physical aging below T_g (Chapter 3.2). Within the framework of irreversible thermodynamics, the issue of entropy at the glass transition is then examined by P. Gujrati who shows how both communal entropy and free volume vanish at an *ideal* glass transition where the viscosity divergence would take place (Chapter 3.3).

Following these theoretical accounts, three chapters consider specific physical properties. In the first, B. Hehlen and B. Rufflé deal with the various modes of vibrations existing in glasses, paying particular attention to the low temperatures at which the boson peak represents an excess of vibrational modes with respect to those predicted by the Debye model for crystals (Chapter 3.4). Of direct practical interest, the densities of glasses and melts and their temperature and pressure derivatives are then reviewed by M. Toplis who also presents empirical models predicting these properties as a function of chemical composition (Chapter 3.5). A similar approach is followed by P. Richet and D. de Ligny in the next chapter, which is mainly devoted to heat capacity and entropy from near 0 K to superliquidus temperatures: at lower temperatures, the properties of *glasses* are exclusively vibrational and mainly determined by the oxygen coordination of cations, whereas the picture is markedly more complicated above the glass transition by configurational contributions to the properties of *liquids*, whose nature remains largely elusive (Chapter 3.6).

After these overviews of key physical properties, the ground is ready for a thorough discussion of relaxation processes. Relying mainly on calorimetric measurements, U. Fotheringham describes how the concept of fictive temperature can be incorporated into various relaxation models to

predict accurately features of great practical interest such as thermal shrinkage and index of refraction changes as a function of time and temperature (Chapter 3.7). Because of extreme metastability, a special case of relaxation is that of glasses quenched at rates of the order of 10^6 K/min. As revealed by calorimetric experiments examined by Y. Yue, these *hyperquenched* glasses do show unusual features related to structural heterogeneities and to the existence of fragile-to-strong rheological transitions in glass-forming systems (Chapter 3.8).

The existence of polyamorphism, i.e. transitions from one amorphous phase to another, has recently been an unexpected discovery because the structure and properties of glasses were instead thought to vary continuously as a function of the quench temperature and pressure. As reviewed by P. McMillan and M. Wilding, these abrupt phase changes akin to first-order transitions in crystals have been extensively investigated and their origin accounted for in terms of the topology of configurational-energy landscapes (Chapter 3.9). Amorphous phases can also be prepared by high-pressure compression of crystals that undergo structural collapse when their elastic limits are exceeded. As explained again in terms of configurational-energy landscape by P. McMillan, D. Machon, and M. Wilding, the similarity of these phases with the dense polyamorphs formed at high pressures is not fortuitous (Chapter 3.10).

From the standpoint of mechanical stability, amorphous phases display a much greater variety of compression mechanisms than crystals, thanks to the lack of structural constraints imposed by the symmetry of a crystal lattice. In addition, the intrinsic strength of glasses should in principle be limited only by that of interatomic bonds since it is not reduced by grain boundaries. As explained by R. Hand, however, the actual strength is hundred times smaller because of the existence of surface flaws where the accumulation of stresses triggers breakage; whereas the abundance of flaws increases with time and their effects have to be treated statistically, their creation can be limited in various ways (Chapter 3.11). Strategies for strengthening glass are described in more detail by S. Karlsson and L. Wondraczek; in addition to elimination of flaws by mechanical polishing or flame finishing, these involve the creation of compressive stresses at the glass surfaces by either physical or chemical means, i.e. tempering by rapid, homogenous cooling (Figure 1) or exchange of smaller by bigger ions, e.g. replacement of Na^+ by K^+ (Chapter 3.12). Irradiation by energetic photons or subatomic particles is another source of defects reviewed by N. Ollier, S. Girard, and S. Peugeot who describe their effects on optical and mechanical properties and the ways in which these can be reduced (Chapter 3.13).

The last chapter is devoted to the special case of amorphous ices, which have recently received much attention not so much because of their cosmochemical importance, but because they are prime illustrations of polyamorphism. Their formation and properties are thus reviewed by R. Tournier who goes into the details of a thermodynamic model of nucleation and growth

originally designed for crystals – including numerical applications – to account for the formation of these amorphous ices and, in addition, to throw valuable light on the general problem of the glass transition in terms of transformations between supercooled liquids of different densities (Chapter 3.14).

3.1

Glass Formation

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1 Introduction

Glasses can be formed by various methods, including physical vapor deposition, solid-state reactions, thermochemical and mechanochemical treatments, or liquid-state reactions with sol–gel techniques (Chapter 8.1). Amorphous solids can also be prepared under the action of high pressure (Chapter 3.10) or by irradiation of crystals (Chapter 3.13). In industry or in Nature (Chapters 7.1 and 7.2), however, vitrification most frequently relies on the extremely strong viscosity increases when melts are cooled until the glass transition eventually takes place before nucleation and crystal growth have developed (Chapter 5.4). The topic dealt with in this chapter will thus be glass formation by melt cooling.

In a first approximation, the glass transition is conveniently characterized by a single parameter, the glass transition temperature T_g (Chapter 3.2). Under typical cooling rates of the order of 10 K/s, the standard T_g is the temperature at which the viscosity is about 10^{12} Pa.s (10^{13} P) at the macroscopic observational timescales of 10^2 – 10^3 seconds that are relevant to actual glass formation. As defined in this way, T_g is always significantly lower than the melting (or liquidus) temperature T_m . It can be roughly estimated with the Kauzmann formula $T_g \approx 2T_m/3$ [1].

In principle, any liquid vitrifies if the melt is cooled sufficiently fast to prevent crystallization from happening. This is by definition the case of the vast bulk of

commercially used glasses, which are made up of oxides. In glass technology, SiO_2 , GeO_2 , B_2O_3 , and P_2O_5 are archetypal *glass formers* in that they easily form glass networks by themselves or in combination with other oxides. But in practice it is not obvious to predict which materials readily vitrify and under what conditions they do so. As a matter of fact, the high viscosities that favor vitrification are related to structural factors whereas configurational complexity also contributes to frustrate crystallization. Here, particular attention will thus be paid not only to the kinetics of vitrification and its theoretical aspects but also to these factors.

In preamble, however, it is useful to examine the way in which glass is defined because of the possibly surprising fact that there is no generally accepted definition of this state of matter. Likewise, a few fundamental points will be summarized about relaxation, the process by which the structure and properties of an amorphous substance tend to reach their equilibrium values to vanish below the glass transition (Chapter 3.7).

Acronyms

BO	bridging oxygen
CCR	critical cooling rate
CN	coordination number
CPT	configuron percolation theory
DSC	differential scanning calorimetry
DTA	differential thermal analysis
ICG	International Commission on Glass
IUPAC	International Union of Pure and Applied Chemistry
NBO	non-bridging oxygen
TTT	time temperature transformation

Reviewers: R. Hand, Department of Materials Science and Engineering, University of Sheffield, Sheffield, UK
V. Stolyarova, Saint Petersburg State University, Saint Petersburg, Russian Federation

2 Glass and Relaxation

According to the International Commission on Glass (ICG, Chapter 9.11), a glass is a homogeneous amorphous solid material produced when a viscous molten material is cooled rapidly enough through the glass transition range without leaving sufficient time for the formation of a regular crystal lattice. As for the International Union of Pure and Applied Chemistry (IUPAC), its Compendium of Chemical Terminology puts instead the emphasis on the process through which a glass is produced by defining it as a second-order transition taking place upon cooling of a supercooled melt [2]. Additionally, IUPAC states that below T_g the physical properties of glasses vary in a manner like those of crystalline phases.

Of more serious consequences that this divergence is the fact that the nature of the glass transition is not yet well understood in spite of its fundamental importance (Chapter 3.3). One reason is the almost undetectable structural differences noted between the supercooled liquid and glass phases, which contrast with the marked changes observed in mechanical and other physical properties associated with the extremely large changes in the timescale of relaxation processes at T_g and below.

Specifically, a glass has a topologically disordered distribution of atoms or molecules, like a liquid, but it has also the elastic properties of an isotropic solid. Moreover, the translation-rotation symmetry at T_g is unchanged as the glass retains the topological disorder of the fluid from which it formed. This symmetry similarity of both liquid and glassy phases generally leaves unexplained the basic differences observed between their properties. An exception is the qualitative difference that has been demonstrated in the symmetries of liquid and glasses in terms of Hausdorff dimensionality for the system of bonds which shows a stepwise change exactly at T_g [3]. The reason is that broken bonds in glasses are present as point defects, thus forming a set of zero-Hausdorff dimensionality, whereas in liquids just above the T_g they are associated in macroscopic percolating clusters that form sets characterized by the Hausdorff dimensionality ≈ 2.5 [3].

Although glasses are metastable materials with respect to isochemical crystals, their transformation to a thermodynamically stable crystalline structure is kinetically impeded. The metastability of silicate glasses commonly produced industrially is not a practical concern as most of them are stable for times much longer than any imaginable timescales of use. In practice, that there is no stress relaxation at room temperatures is indicated by the fact that high permanent internal stresses are preserved in glass articles made more than several millennia ago, and even in billion-year-old extraterrestrial glasses (Chapter 7.1).

The reason for this stability is that relaxation processes are controlled by viscosity. The characteristic time τ required to achieve time-independent parameters can be derived from Maxwell's simple relaxation model, which predicts that $\tau = \eta/G$, where G is the shear modulus and η the viscosity (Chapter 3.7). The higher the viscosity, the longer the relaxation time. Besides, viscosity changes are thermally activated. Glass-forming oxides are characterized by high activation energies and very high viscosities under normal conditions. As an extreme example, fused silica has an activation energy for viscous flow of Q_H of 759 kJ/mol at lower temperatures and a shear modulus of about 31 GPa, which implies relaxation times τ_M as long as 10^{98} years at room temperature, an immeasurably longer time than even the $14 \cdot 10^9$ years lifetime of the universe.

3 Kinetic Theory of Vitrification

As already stated, vitrification on cooling is tantamount to bypassing crystallization, which would bring the material to an ordered state of matter of lower energy and, thus, of greater stability. If cooled quickly enough, virtually any material can vitrify. Hence, an important question is to know how fast the melt should be cooled to avoid detectable crystallization. Actually, the cooling rates of good glass formers range from 1 to 10 K/s and those of poor ones are higher than ~ 100 K/s. Familiar glass-forming materials such as SiO_2 -rich silicates thus do not require fast cooling. An extreme example is supercooled $\text{NaAlSi}_3\text{O}_8$, which did not crystallize at all after five years spent 90 K below the melting point of the albite feldspar mineral [4]. Even though the quenching rate of a liquid medium can be increased to about 10^3 K/s, such high values may not be fast enough to avoid partial or complete crystallization. In silicates, SiO_2 -poor olivine compositions (e.g. Mg_2SiO_4) are notorious examples of liquids that are difficult to vitrify at such rates [5]. Quickly crystallizing liquids such as metals may require still faster cooling. For instance, early metallic glasses (Chapter 7.10) had to be splat quenched in the form of thin ribbons at about 10^6 K/s to avoid crystallization, mainly because their viscosities remain very low with decreasing temperatures (Figure 1).

An added complication is that melts can be good glass formers only within limited composition regions as indicated in Figure 2 for aluminosilicates. Compilations of glass-forming regions of phase diagrams are available [6–8]. As a rule, however, glass formation is enhanced in more complex systems. Oxide systems containing a variety of cations are easier to obtain in a glassy state as their liquidus temperature is lower and their complexity

Figure 1 Critical cooling rates for glass formation. Reduced glass transition temperature T_g defined as T_g/T_m , where T_m is the liquidus temperature.

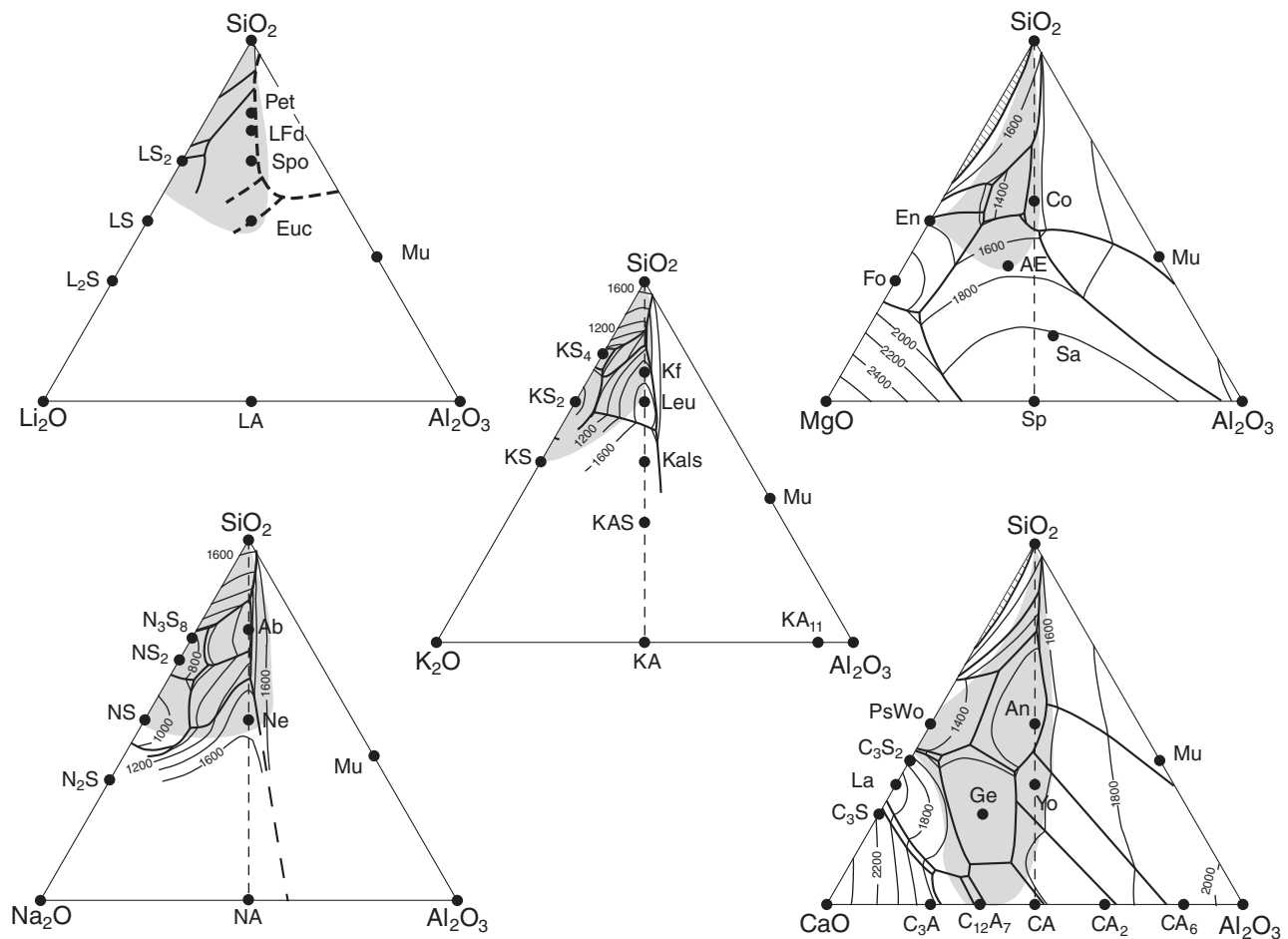
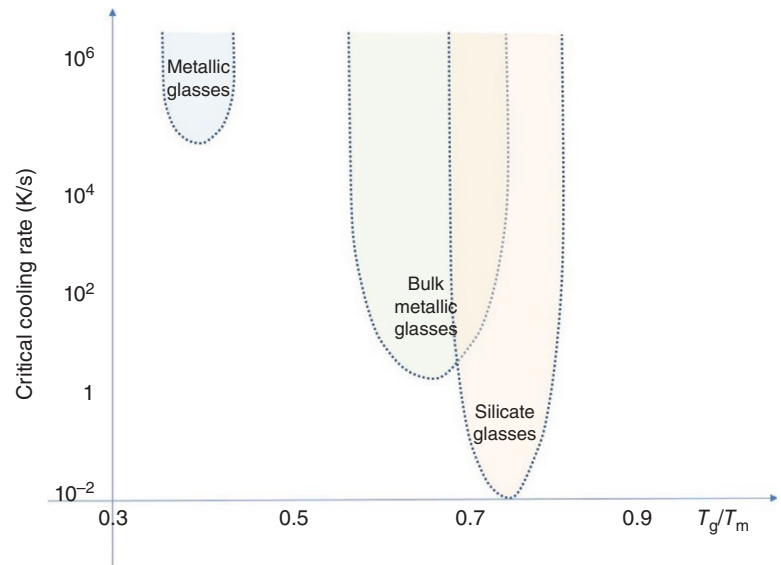


Figure 2 Glass formation ranges in aluminosilicate systems (shaded areas). *Source:* After [6], courtesy P. Richet.

necessitates longer times for diffusion-controlled redistribution of their diverse constituents before crystal nucleation and growth can take place.

If crystallization is bypassed, the melt undergoes the glass transition in a temperature range that shifts to higher temperatures for higher cooling rates. Both the width of this range and the value of T_g within it may vary by typically several tens of degrees. As the width and variation are small compared with T_g , it is therefore possible to manage a cooling schedule rapid enough to keep the degree of crystallization negligible. Volume fractions considered to be negligible are lower than 1 ppm, which is the typical instrumental limit for detecting the presence of crystals by microanalytical techniques (Chapter 2.3).

If ν designates the volume fraction of crystalline(s) phase(s), the material is amorphous if $\nu = 0$, crystalline if $\nu = 1$, and polyphase or heterogeneous when $0 < \nu < 1$. Under isothermal conditions the volume fraction of a growing crystalline phase varies with time as described by the Johnson–Mehl–Avrami–Kolmogorov equation (see [9] for references and details):

$$\nu = 1 - \exp \left[-\frac{\pi}{3} I_\nu u^3 t^4 \right], \quad (1)$$

where u is the rate of crystal growth and I_ν the nucleation rate.

If both rates can be estimated, the volume fraction of the crystalline phase ν achieved for a given cooling rate can be calculated and the results be compared with experimental data. The rate of homogeneous nucleation is given by James equation:

$$I_\nu = \frac{n_\nu k_B T}{3\pi\lambda^3 \eta} \exp \left[-\frac{W^*}{k_B T} \right]. \quad (2)$$

Here W^* is the thermodynamic barrier to homogeneous nucleation, n_ν the number of molecules or formula units of nucleating phase per unit volume, λ a jump distance, and η viscosity. For heterogeneous nucleation, the thermodynamic barrier to nucleation actually becomes $W_{h*} = W^*(2 + \cos\theta)(1 - \cos\theta)^2/4$, where θ is the contact angle between the crystal and the nucleating heterogeneity. The rate of crystal growth is given by Wilson–Frenkel equation:

$$u = \frac{fD_c}{\lambda} \left[1 - \exp \left[-\frac{\Delta G_\nu V_m}{RT} \right] \right], \quad (3)$$

where f is the interface site factor, D_c the kinetic (diffusion) coefficient, V_m the molar volume, and ΔG_ν the difference in Gibbs free energy between unit volumes of the crystal and liquid.

One then obtains the critical cooling time (t_c) and rate (q_c), for a defined volume fraction of crystals ν_c . Taking the aforementioned value ν_c of 1 ppm, one obtains

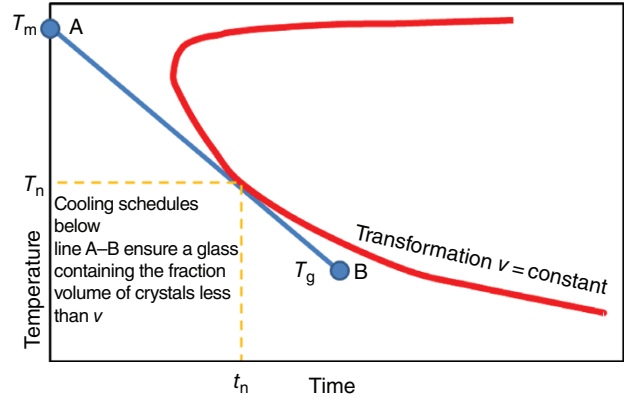


Figure 3 Determination of the critical cooling rate from a time temperature transformation diagram.

$$t_c = \left(\frac{3\nu_c}{\pi I_\nu u^3} \right)^{1/4} \quad (4a)$$

and

$$q_c = \frac{(T_m - T_g)}{t_c} \approx \frac{T_m}{3t_c}. \quad (4b)$$

Despite its general correctness and qualitative agreement with experiments, the kinetic theory suffers from limited quantitative applications. Whereas quantitative agreement has been achieved for simple silicate systems, the discrepancy is of many orders of magnitude in most cases [6, 8].

In practice, the critical cooling rate (CCR) is determined from the so-called time temperature transformation (TTT) diagrams, which represent nose-shaped curves with a constant crystal fraction on time–temperature axes (Figure 3). To ensure the obtention of a glass with a crystal volume fraction lower than ν , it is required to follow a cooling pathway such that the cooling line (curve) will not touch the nose [10]. The CCR is then found as follows:

$$q_c = \frac{(T_m - T_n)}{t_n}. \quad (5)$$

Examples are listed in Table 1.

4 The Viscosity Factor

The definition of the glass transition in terms of the standard glass transition derived from the viscosity–temperature relationship, $\eta(T)$, is not thermodynamic, but operational [8]. As determined from changes in second-order derivatives of thermodynamic variables, the glass transition takes place at viscosities in the range 10^8 – 10^{13} Pa s depending on the cooling rate. In view of

Table 1 Critical cooling rate for some glasses, K/s.

Material	Nucleation mechanism			
	Homogeneous	Heterogeneous $\theta = 100^\circ$	Heterogeneous $\theta = 60^\circ$	Heterogeneous $\theta = 40^\circ$
SiO ₂	9×10^{-6}	10^{-5}	8×10^{-3}	2×10^{-1}
GeO ₂	3×10^{-3}	3×10^{-3}	1	20
Na ₂ O 2 SiO ₂	6×10^{-3}	8×10^{-3}	10	3×10^2
Salol [C ₁₃ H ₁₀ O ₃]	10			
Water	10^7			
Ag	10^{10}			

Source: After [9].

the very steep temperature dependence of viscosity, a great difference in this parameter results in only small variations of the operational T_g .

As has long been recognized, glass formation is therefore easier in eutectic regions because freezing-point depressions enable lower temperatures and higher viscosities to be reached [11]. However, viscosity at the liquidus is not a single scaling parameter for assessing glass-forming ability. The temperature dependence of the viscosity below T_m must also be considered because vitrification takes place much below the liquidus [6, 8].

Viscous flow in glass-forming liquids is characterized by deviations from Arrhenius laws with an activation energy Q that decreases from a high Q_H near the glass transition to a low Q_L at superliquidus temperatures. As a fragility index characterizing the temperature dependence of viscosity, Doremus [12] has proposed the ratio:

$$R_D = \frac{Q_H}{Q_L}. \quad (6)$$

Short (or fragile) and long (or strong) glass melts are, therefore, characterized by R_D values higher and lower than 2, respectively.

Many equations have been proposed to express viscosity–temperature relationships (Chapter 4.1, [13–15]). Consistent with Doremus criterion, an exponential expression with activation energies Q_L and Q_H at low and high temperatures, respectively, [13] will be used here because it results from the configuron percolation theory (CPT), which accounts for viscous flow in terms of elementary excitations resulting from broken bonds named *configurons* [14, 16]. This equation (Sheffield model) is

$$\eta(T) = A_1 T \left[1 + A_2 \exp\left(\frac{B}{RT}\right) \right] \left[1 + C \exp\left(\frac{D}{RT}\right) \right], \quad (7)$$

where $A_1 = k/6\pi r D_0$, $A_2 = \exp(-S_m/R)$, $B = H_m$, $C = \exp(-S_d/R)$ and $D = H_d$, R the gas constant, k Boltzmann

constant, r the configuron radius $D_0 = fg\lambda^2 zp_0\nu_0$, f the correlation factor, g a geometrical factor ($\sim 1/6$), λ the average jump length, ν_0 the configuron vibrational frequency or the frequency (with which the configuron attempts to surmount the energy barrier to jump into a neighboring site), z the number of nearest neighbors, p_0 a configuration factor, H_d the enthalpy, S_d the entropy of formation, and H_m and S_m the enthalpy and entropy of motion of the configurons.

In practice, one finds that $A_2 \exp(B/RT) \gg 1$, i.e. that four parameters usually suffice for Eq. (7) to be fitted to practically all available experimental viscosity data [17]. Comparison with other viscosity models and numerical calculations have confirmed the excellent description of the viscosity provided by Eq. (7) for simple and complex organic and inorganic compositions (e.g. [13]). This equation can be readily approximated within narrow temperature intervals by expressions derived from the well-known Vogel-Tammann-Fulcher, Adam–Gibbs, Avramov–Milchev, or Sanditov models [14, 15, 17]. It can be used at all temperatures and gives the correct Arrhenius-type asymptotes at high and low temperatures, namely $\eta(T) \sim \exp(Q_H/RT)$ at $T \ll T_g$, and $\eta(T) \sim \exp(Q_L/RT)$ at $T \gg T_g$, where $Q_H = H_d + H_m$ and $Q_L = H_m$. Obviously, the activation energy of viscosity reduces to a low value equal to H_m at high temperatures when temperature fluctuations create plenty of configurons. In contrast, some bonds need to be broken in the glassy state as temperature fluctuations do not create them effectively so that the activation energy then takes its full value $Q_H = H_d + H_m$.

5 Structural Factors

Apart from inhomogeneities and potential phase separation, glasses lack long-range order but do possess short- and medium-range ordering (Chapter 2.1). A number of models have aimed at revealing the most characteristic

structural aspects of good glass formers. The most noted structural criterion for ready glass formation, i.e. at rates q_c lower than 10 K/s, is based on Zachariasen theory in which the oxide glasses A_mO_n are assumed to be 3-D networks obeying four rules: (i) the oxygen is linked to two atoms of A; (ii) the oxygen coordination number around A is three or four; (iii) the cation polyhedra share corners; and (iv) at least three corners are shared [18]. This theory is referred to as crystallochemical, but was applicable only to oxide glasses in its original form; it led to the so-called 3-D continuous random network (CRN) model (Chapter 2.1). With respect to a glass and its isochemical crystal, the basic postulates of CRN are that: (i) interatomic forces are similar in both phases; (ii) the glass is in a slightly higher energy state; (iii) nearest-neighbor coordination polyhedra are similar; and (iv) the nature of interatomic bonds is also similar.

The strong points of Zachariasen's model are that it predicts the existence of the main oxide glass formers (SiO_2 , GeO_2 , B_2O_3 , P_2O_5 , etc.) and glass modifiers (Na_2O , CaO , etc.) and makes room for the distinction between bridging (BO) and non-bridging oxygens (NBO). Its main limitation is that it does not consider at all modified oxides or multicomponent systems, or even non-oxide glasses. In addition, several exceptions to its rules are found as exemplified by alumina-lime glasses and chain-like glass structures (e.g. metaphosphate glasses).

Smekal [19] thus developed the concept of the mixing bond nature of (good) glass formers. He noted that pure covalent bonds are incompatible with a random arrangement in view of sharply defined bond lengths and angles. Purely ionic or metallic bonds lack any directional characteristics so that the presence of *mixed* chemical bonding is necessary for glass formation. Indeed, known glass formers obey this concept: (i) inorganic compounds like SiO_2 or B_2O_3 where the A–O bonds are partly covalent and partly ionic; (ii) elements (S, Se) having chain structures with covalent bonds within the chain and van der Waal's forces between them (Chapter 6.5); and (iii) organic compounds containing large molecules with covalent internal bonds and van der Waals' forces between the molecules (Chapter 8.8).

Alternatively, Stanworth proposed a criterion for glass formation according to which the electronegativity of cations in oxide glasses falls within a certain range between 1.90 and 2.20 [20]. Although the electronegativity values of the constituent atoms can be used to predict the formation of many glasses, this criterion cannot account for systems when bond strength needs to be considered as a secondary criterion.

Sun developed the bond-strength model on the assumption that, when a melt vitrifies, the stronger the metal–oxygen bond, the more difficult the structural

rearrangements necessary for crystallization become and, hence, the easier is glass formation. Glass formation is then ensured by the connectivity of bridging bonds combined with strong bonding between atoms (ions) [21]. Sun thus classified oxides according to their bond strengths so that glass formers form strong bonds with oxygen to yield a rigid network, which results in a high viscosity. He defined modifiers as weakly bonding with oxygen in such a way that they disrupt and modify the network. Without producing glasses on their own, they do form intermediate bonds with oxygen and thus aid vitrification with other oxides.

In practical terms, Sun's energy criterion establishes a correlation between the glass-forming tendency and the strength of the bond between the elements and the anion in the glass. The single bond strength E_b was defined as:

$$E_b = \frac{E_d}{CN}, \quad (8)$$

where CN is the coordination number and E_d the dissociation energy of oxides into their gaseous elements. For B_2O_3 , SiO_2 , GeO_2 , P_2O_5 , or Al_2O_3 , the single bond strength of network formers with oxygen is higher than 330 kJ/mol. Values lower than 250 kJ/mol hold for network modifiers such as Li, Na, K, Mg, or Ca whereas intermediate cations such as Ti, Zn, and Pb are characterized by values intermediate between these two figures.

For both Zachariasen and Sun models Al^{+3} is a challenge. Although Al_2O_3 satisfies Zachariasen's criteria, it does not form a glass. Likewise, with $E_d = 1320$ – 1680 kJ, alumina should be a glass former at a CN of 4 for Al^{3+} and a modifier at a CN of 6. Sun model was also specific to oxides. It did not account for chalcogenide glasses (Chapter 6.5) with typical bond strength of 170 kJ/mol along the chains (covalent bond) and less between the chains (van der Waals forces). An interesting intermediate class of oxide is formed by TeO_2 , MoO_3 , Bi_2O_3 , Al_2O_3 , Ga_2O_3 , and V_2O_5 , which do not vitrify by themselves but will do so when mixed with other (modifier) oxides.

Rawson modified Sun's criteria for glass formation [22] by considering the ratio of the bond strength and energy available at the melting point T_m instead of the coordination number. He noted that glass formation then correlates better with E_b/T_m , being achieved for values of this ratio higher than 0.05 kJ/mol K. The higher this value, the lower the probability for bonds to be broken at T_m , and hence the greater the vitrifiability. Glass formation is thus easier for high bond strength and low melting (liquidus) temperature, which implies that eutectic compositions do favor it.

Based on Rawson and Sun approaches, a modified glass-forming criterion termed the *Thermodynamic Relative Glass-Forming Ability* has recently been proposed in terms of the parameter $E_b/C_p T_m$, where C_p is the isobaric

heat capacity [23], which can be regarded as an extension of Rawson's criteria. The ordering that results from this model is not convincing, however, and its basic ideas remain to be well justified.

Dietzel [24] characterized the ability of cations to enter the network structure by their field strength, which he defined as

$$F = \frac{Z}{r^2}, \quad (9)$$

where Z is its valence and r its ionic radius ($\text{\AA}$) in the oxide. As listed in Table 2, lower field-strength cations (e.g. alkalis) are network modifiers, whereas ions with higher field strengths (such as Si, P, or B) are network formers. Interestingly, Dietzel model is appropriate for describing phase separation, either through crystallization or unmixing, in cooled binary systems such as $\text{SiO}_2\text{--P}_2\text{O}_5$, $\text{SiO}_2\text{--B}_2\text{O}_3$, or $\text{B}_2\text{O}_3\text{--P}_2\text{O}_5$. This may generally be the case when the field strengths of two cations are approximately equal since forming a single stable crystalline compound normally requires a difference ΔF greater than 0.3. The number of possible stable compounds increases with ΔF as well as the tendency to form glass. For a binary system, glass formation is likely for Δf larger than 1.33 although this theory is useful to categorize the glass-forming ability of conventional systems, but not universally [25].

Finally, the topological constraints theory introduced by Phillips [26] must also be mentioned. As reviewed in Chapter 2.7, it indicates that the glass-forming tendency is maximized when the number of constraints is equal to the number of degrees of freedom in the structure.

In summary, vitrification is favored by high viscosity and configurational complexity. A more complicated chemical composition translates into a greater number of compounds that could nucleate. Owing to mutual competition between these possible crystals, nucleation and growth crystals end up being frustrated. That they do not take place upon rapid cooling thus is a consequence of a *confusion principle* [8].

6 Glass-Liquid Transition

Structural theories with energetic and microstructural criteria such as topological constraints describe elements that favor glass formation, i.e. the preservation of a topologically disordered distribution of basic elements in glasses. Kinetic theory shows how to avoid crystallization rather than explaining why the vitreous state really forms through the liquid–glass transition – it is at T_g that the “drama” occurs! Although kinetically controlled, the glass transition manifests itself as a second-order phase

transformation in the sense of Ehrenfest classification. Depending on the kind of measurement performed, it is thus revealed either as a continuous change of first-order thermodynamic properties such as volume, enthalpy, entropy, or as a discontinuous variation of second-order thermodynamic properties such as heat capacity or thermal expansion coefficient across the glass transition range.

As indicated by its name, the CPT treats the glass transition as a percolation-type second-order transformation [27]. It pictures it as the disappearance in the glassy state of percolating clusters of broken bonds – configurons. Above T_g , percolating clusters, which are formed by broken bonds, enable a floppier structure and hence a greater degree of freedom for atomic motion so that it results in a higher heat capacity and thermal expansion coefficient. Below T_g there are no extended clusters of broken bonds such that the material has acquired a 3-D structure with a bonding system similar to that of crystals except for lattice disorder. This disordered lattice then contains only point defects in the form of configurons. Agglomerates of fractal structures made of these broken bonds are present only above T_g , which is given by:

$$T_g = \frac{H_d}{S_d + R \ln [(1 - \phi_c)/\phi_c]}. \quad (10)$$

In this equation H_d and S_d are the quasi-equilibrium (isostructural) enthalpy and entropy of configurons present in Eq. (7) and ϕ_c is the percolation threshold, i.e. the critical fraction of space occupied by spheres of bond-length diameters located within the bonding sites of the disordered lattice.

For strong melts such as SiO_2 , the percolation threshold in Eq. (10) is given by the theoretical (universal) Scher–Zallen critical density ϕ_c of 0.15 ± 0.01 , which results in a practical coincidence between the calculated and measured T_g values. The parameter H_m has no influence on T_g as it characterizes the mobility of atoms or molecules through the high-temperature fluidity of the melt – see Eq. (7). Because H_d is half of bond strength (Table 2), Eq. (10) shows that the higher this strength, the higher T_g . The vacancy model of the generalized lattice theory of associated solutions provides direct means to calculate thermodynamic properties as well as the relative number of bonds formed in glasses and melts when the second coordination sphere of atoms is taken into consideration [28].

In terms of chemical bonds, an amorphous material transforms to a glass on cooling when the topology of connections changes (Table 3), i.e. when the Hausdorff dimensionality of broken bonds changes from the 2.5 value of a fractal percolating cluster made of broken bonds to the zero value of a 3-D solid. In terms of bonding lattice, the

Table 2 Classification of cations according to Diezel's field strength.

Element	Valence Z	Ionic distance for oxides, Å	Coordination number	Field strength, 1/Å ²	Bond strength, kJ/mol	Function
Si	4	1.60	4	1.57	443	Network formers: <i>F</i> ~1.5–2.0
B	3	1.50	3	1.63	498	
	4		4	1.34	372	
P	5	1.55	4	2.1	368–464	
Ti	4	1.96	4	1.25	455	Intermediates: <i>F</i> ~0.5–1.0
	4	1.96	6	1.04	304	
Al	3	1.77	4	0.96	335–423	
	3	1.89	6	0.84	224–284	
Fe	3	1.88	4	0.85		
	3	1.99	6	0.76		
Be	2	1.53	4	0.86	263	Network modifiers: <i>F</i> ~0.1–0.4
Zr	4		6	0.84	338	
	4	2.28	8	0.77	255	
Mg	2	2.03	4	0.53		
	2	2.10	6	0.45	155	
Pb	2		6	0.34	310	
	2	2.74	8	0.27	151	
Ca	2	2.48	8	0.33	134	
Sr	2	2.69	8	0.28	134	
Li	1	2.10	6	0.23	151	
Na	1	2.30	6	0.19	84	
K	1	2.77	8	0.13	54	
Cs	1		12	0.10	42	

Table 3 Hausdorff dimensionality of the bonding system at glass transition.

Amorphous material	Below T_g (glasses)	Above T_g (supercooled melts)
Broken bonds – configurons	0	2.5 ^a
Chemical bonds backbone cluster	3	3
Chemical bonds	3	2.5 ^a

^a Experimental dimensionality – 2.4–2.8.

transition from the glass to the liquid upon heating may be explained as a reduction of the topological signature (i.e. Hausdorff dimensionality [29]) of the disordered bonding lattice from 3 for a glass (3-D bonded material) to the fractal D_f of 2.4–2.8 of the melt. These are the main changes that account for the drastic variations in material properties at glass-to-liquid transition [27].

Most experimental T_g data have been obtained by differential thermal analysis (DTA), differential scanning calorimetry (DSC), or dilatometry [30], where T_g is generally defined as the temperature at which the tangents to the glass and liquid curves of the relevant property intersect (Chapter 3.2). Heating (cooling) rates for DTA/DSC measurements are typically as high as 10 K/min whereas they are in 3–5 K/min range in dilatometry. As already stated, the glass transition is not abrupt but typically occurs over a few tens of degrees. For not very high cooling rates (q), its dependence on q is given by the Bartenev–Ritland equation:

$$\frac{1}{T_g} = a_1 - a_2 \ln q, \quad (11)$$

where a_1 and a_2 are empirical constants. Although Eq. (11) also results from CPT, it should be replaced by a generalized version at high cooling rates [31]. In addition, CPT predicts that the transition takes place not as a sharp discontinuity, but over a finite temperature

interval where the properties of the material depend on time as well as on thermal history.

Following the analysis of [8], we may ask why viscous liquids eventually vitrify instead of remaining in the supercooled liquid state when they escape crystallization. One answer to this question is purely kinetic and relies only on increasingly long relaxation times or increasing viscosities on cooling. The glass transition would result only from the limited timescale of feasible measurements so that any glass would eventually relax to the equilibrium state if experiments could last forever. In fact, a simple thermodynamic argument proposed by Kauzmann [32] indicates that this answer is incorrect. The reason originates in the existence of a configurational contribution that causes the heat capacity of a liquid to be generally higher than that of a crystal of the same composition. As a consequence, the entropy of the liquid decreases on cooling faster than that of the crystal (Figure 4).

If the entropy of the supercooled liquid were extrapolated to temperatures much below T_g , it would become lower at a temperature T_K than that of the crystal. Because it is unlikely that an amorphous phase could ever have a lower entropy than an isochemical crystal, the conclusion known as Kauzmann's paradox is that an amorphous phase cannot exist below T_K . The temperature of such an entropy catastrophe constitutes the lower bound to the metastability limit of the supercooled liquid. As internal equilibrium cannot be reached below T_K , the liquid must undergo a phase transition before reaching this temperature. This is, of course, the glass transition, and Kauzmann's paradox suggests that, although it is kinetic in nature, it anticipates a thermodynamic transition. In other words, CPT treats the glass transition as

a true phase transformation although as a nonequilibrium one. The liquid transforms in a continuous way into a glass, which behaves mechanically as a crystalline solid when the motions of atoms become very much frustrated below T_g where the extensive clusters of broken bonds of the liquid are no longer present. The degree of frustration then is actually the same as in a 3-D crystalline material so that the heat capacity does not show the same high rate of change as in the liquid. This feature is clearly seen both in experiments and as an outcome of the CPT concept (Figure 5). Importantly, CPT yields a universal law for

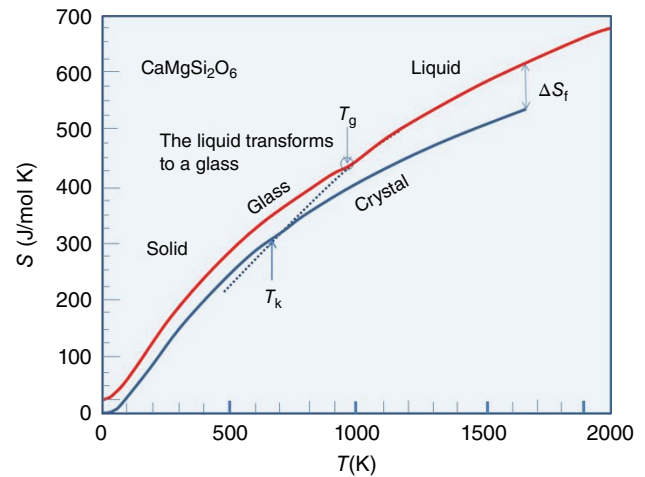


Figure 4 Entropy of the amorphous and crystalline phases of diopside, $\text{CaMgSi}_2\text{O}_6$. Source: After [8]. The liquid transforms into a glass below T_g , therefore the entropy of condensed phase (upper curve) does not follow the dashed line which is an extension of liquid entropy curve below T_g .

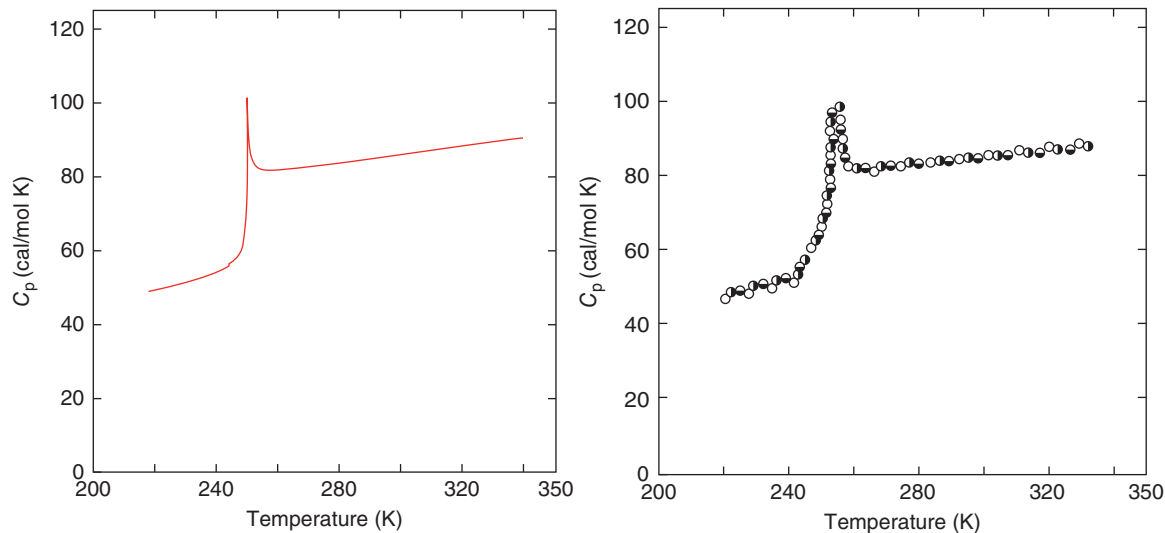


Figure 5 Comparison between the heat capacities of amorphous *o*-terphenol measured and calculated with configuron percolation theory. Source: After [3].

susceptibilities such as heat capacity or thermal expansion near T_g [3, 27]:

$$C_p, \alpha \propto \frac{1}{|T - T_g|^{0.59}}. \quad (12)$$

A last feature deserving to be mentioned is the “universal” dependence of the light scattering intensity on the time after a temperature jump in the glass transition range of oxide glasses, which is known as the Bokov effect [33]. The intensity displays a maximum whose height and location on the timescale depends on the previous history of the glass. The Bokov effect is associated with nonequilibrium fluctuations produced by coupling between hydrodynamic modes. Detailed investigations in the past decade have demonstrated that similarities observed in the glass transition region of oxides and polymers account for structural transformations related to the formation of spatially extensive structures, which in turn could be related to clustering effects similar to that envisaged by CPT and other similar models. The Bokov effect thus is providing additional arguments to characterize the glass transition as a second order like phase transformation rather than simply as a slowing down of dynamic processes.

7 Perspectives

Understanding vitrification mechanisms is of great importance either practically or theoretically. Although progress made in this respect has been very impressive, many of the questions remain unresolved. Among them, a central one is that of the glass transition itself, which has a pronounced relaxational, kinetic character in spite of its similarity with a second-order phase transition in the Ehrenfest sense with volume and entropy continuity, but discontinuities of their derivatives that are used in practice to detect T_g . Discussion about the nature of glass continues. After some lull it has gathered new momentum, especially in the second decade of the new century as the microscopic mechanisms generating the glassy state of matter are still debated. Future developments could be based on computer modeling that does also show the appearance of discontinuities in derivative thermodynamic parameters at the glass transition.

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3.2

Thermodynamics of Glasses

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1 Introduction

Thermodynamics states that the properties of a system in equilibrium depend neither on time nor on past history. Glasses clearly violate this postulate. Not only do their properties depend on history but they also vary with time at temperatures at which relaxation toward internal thermodynamic equilibrium does occur, but at a rate slow enough to be observable at the timescale of the experiment performed. To deal with glasses, thermodynamics must thus consider nonequilibrium states and their actual cause, namely the irreversibility of the transition that occurs when relaxation times eventually become much longer than experimental timescales such that the material freezes in as a glass.

Much attention is currently paid to the processes driving the glass transition at a microscopic scale and also to their implications for the macroscopic properties of glasses. Because this topic is extensively discussed in this chapter, we will deal here with a second fundamental issue, namely that of the phenomenological approaches followed to understand the observable macroscopic properties of glasses and, thus, to design new applications. To quote a single example, density gradients in tempered glasses are the key to thermal strengthening, which is achieved irreversibly upon cooling (Chapter 3.12).

In this chapter, the basic concepts of macroscopic nonequilibrium thermodynamics will first be summarized and illustrated with experimental heat capacities for a model system, PolyVinylAcetate [PVAc, $(C_4H_6O_2)_n$]. The basic concepts of equilibrium and nonequilibrium will then be introduced to point out why glasses challenge

the laws of thermodynamics. Next, properties of the supercooled liquid state above T_g will be presented and the phenomenology of the glass transition examined in the light of calorimetric data, in particular in terms of configurational properties. The basics of nonequilibrium thermodynamics in the glass transition range will finally be reviewed along with the issue of aging below the glass transition range.

2 Basics of Nonequilibrium Thermodynamics

In thermodynamics one investigates the changes occurring when a system passes from a state A to another state B. At constant chemical composition, the system is in *internal* equilibrium if its state is defined by only two macroscopic variables such as temperature (T), pressure (P), volume (V), enthalpy (H), internal energy (U), or Gibbs free energy (G). Their values are not only constant but independent of the pathway actually followed between any two states A and B. As stated by the First Law of thermodynamics, between A and B the internal energy varies as:

$$\Delta U_{A \rightarrow B} = Q_{A \rightarrow B} + W_{A \rightarrow B}, \quad (1)$$

where $Q_{A \rightarrow B}$ and $W_{A \rightarrow B}$ are the heat and work exchanged by the system with its surroundings, respectively. Likewise, the entropy is decomposed into two parts,

$$\Delta S_{A \rightarrow B} = \frac{Q_{A \rightarrow B}}{T} + \Delta_i S_{A \rightarrow B}, \quad (2)$$

where the first represents the heat exchanged with the surroundings and the second the entropy created within the system itself during the transformation.

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If two equilibrium states are connected by a reversible process, then $\Delta_i S_{A \rightarrow B} = 0$. If the system undergoes instead an irreversible process through which it falls out of equilibrium, then $\Delta_i S_{A \rightarrow B} > 0$ since a spontaneous process is always associated with an entropy increase of the system. Upon glass formation by cooling, pressure increase, or other means, the equilibrium liquid is continuously losing internal equilibrium. As will be discussed here, the question arises as to whether there is any finite production of entropy and – if so – whether this quantity is of importance regarding the other terms involved in the process.

The Third Law of thermodynamics postulates that the entropy of a perfectly ordered system is zero at 0 K. In contradiction with it, however, calorimetric measurements indicate that glasses not only possess nonzero entropies at 0 K but that this *residual entropy* depends on thermal history as illustrated by a simple entropy cycle calculated from measured heat-capacities and entropy of fusion (ΔS_f). Beginning with a perfectly ordered crystal, whose entropy thus is 0 at 0 K, one derives the entropy of the crystal at its congruent temperature of fusion T_f , then that of the melt from this temperature down to the glass transition, and finally that of the glass down to 0 K (Figure 1). The difference S_0 between this entropy and that of the crystal at 0 K is the residual entropy (Table 2), which increases with higher glass transition temperatures and, thus, with higher cooling rates, reflecting the increasingly wide distribution of configurational states obtaining with increasing temperatures.

A finite residual entropy at 0 K might seem to contradict the Third Law of thermodynamics. As justified by Jones and Simon [1], however, there is no contradiction because this law applies only to crystals and other systems in internal equilibrium, which are necessarily ordered at 0 K to minimize their Gibbs free energies. This is not the case of glasses, which do obey the Nernst theorem [2] since they cannot pass from one entropy state to another at 0 K ($\Delta S = 0$ for two neighboring glassy states at 0 K).

Although such determinations also made for partially disordered crystals like ice I_h or CO have long been

explained by simple statistical mechanical models, the very concept of residual entropy has recently been debated [3]. On the assumption that ergodicity must hold for the entropy to be defined, the proponents of a *kinetic* view have claimed that the configurational entropy undergoes an abrupt jump at the glass transition in order to reach the zero value of the crystal entropy at 0 K. In contrast, the proponents of the *conventional* view have stressed that what matters is not time averages but spatial averages of configurational microstates [3], which is the reason why the measured residual entropies do make sense physically and correlate with the specific structural features of glasses and disordered crystals.

By definition, equilibrium thermodynamics cannot alone account for fundamental questions raised when relaxation is too slow with respect to experimental time-scales. Owing to the kinetic nature of the problem, use has been made of the formalism originally developed for the kinetics of chemical reactions by De Donder and his school [4]. With values increasing as the reaction proceeds, a new variable, the advancement of reaction, $\xi(t)$ is defined to characterize the state of the system as a function of time, t , such that the reaction rate is simply $d\xi(t)/dt$. This extensive variable, expressed in mol, accounts for the distribution of matter (local mass or density variation), or the molecular structure, within the system at any time. A new state function, the affinity, A , is then introduced to relate $\xi(t)$ to the driving force of the reaction, its Gibbs free energy (at constant T and P):

$$A(P(t), T(t), \xi(t)) = \left(\frac{-\partial G}{\partial \xi} \right)_{P,T}. \quad (3)$$

The affinity A , expressed in J/mol, is the intensive conjugate variable of ξ . All time dependences are thus embedded into the time variations of the internal parameter ξ , or A , and of the other variables that are controlled experimentally (e.g. T , P).

For a relaxing system, the instantaneous entropy production was simply written by De Donder as the product of the thermodynamic force and the corresponding flux [4],

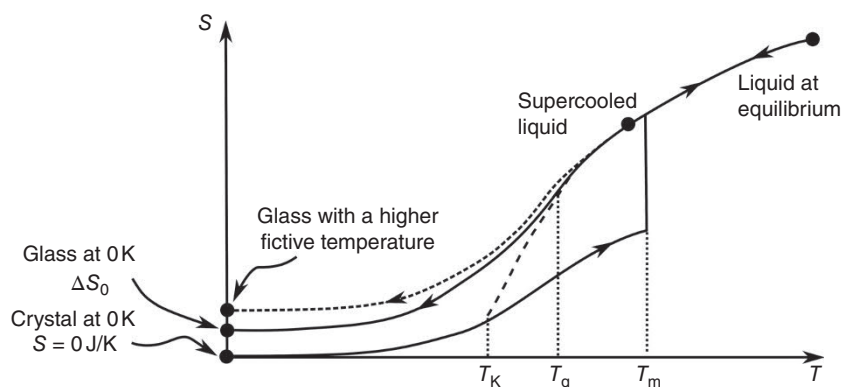


Figure 1 Entropies of the crystal, liquid, supercooled liquid and glass phases of a substance.

Table 1 Thermodynamic states in terms of affinity and its derivatives and in terms of rate of advancement of the process.

Rate of advancement $d\xi/dt$ (extensive, mol/s) Affinity A (intensive, J/mol)	$d\xi/dt = 0$	$d\xi/dt \neq 0$
$A = 0$ and $dA = 0$	True equilibrium; liquid state; $\sigma_i = 0$	Unphysical
$A = 0$ and $dA \neq 0$	Isomassic state; $\sigma_i = 0$	False equilibrium; nonequilibrium state; $\sigma_i = 0$
$A \neq 0$ and $dA = 0$	Isomassic, isoaffine state; $\sigma_i = 0$	Isoaffine state; $\sigma_i \neq 0$
$A \neq 0$ and $dA \neq 0$	Nonequilibrium; glassy state; $\sigma_i = 0$	Nonequilibrium; viscous state; $\sigma_i \neq 0$

Liquid, glass, and relaxing liquid states are indicated by gray cells. The other cells indicate particular states that can be encountered or not during the glass transition. The value of the rate of production of entropy is indicated in each cell.

$$\sigma_i = \frac{d_i S}{dt} = \frac{A}{T} \times \frac{d\xi}{dt}, \quad (4)$$

where the thermodynamic force actually is A/T , for the sake of dimensional analysis (the entropy production being in W/K).

Regarding the glass transition, the problem boils down to know A and ξ (or $d\xi/dt$) and how they evolve with time. Depending on the values of both parameters, however, at this point several cases must be distinguished because not all of them are relevant (Table 1). The first and simplest case is that for which both A and $d\xi/dt$ are zero. It is that of the equilibrium liquid, which will thus be first considered in its metastable, supercooled extension.

3 Supercooled Liquids

Although the liquid state is generally far from simple, it can be considered as an equilibrium reference at viscosities (η) low enough that flow is easy, i.e. at high-enough temperatures at the pressure considered. In that case, the diffusion of microscopic entities, be they molecules or atoms, obeys the Stokes-Einstein relation, which relates the diffusivity D to the temperature and viscosity with:

$$D = \frac{k_B T}{C\eta}, \quad (5)$$

where the coefficient C is a geometrical factor fixed by the boundary condition of the flow.

From its position at time t_0 , a diffusing entity travels a kind of random walk over an average distance $d \sim \sqrt{D(t-t_0)}$ as a function of time. For low-viscosity liquids and high temperatures, D is high so that entities explore a great many different positions and configurations in a time shorter than that needed to perform a physical measurement. They do it through degrees of freedom that include not only thermal motions of translation,

rotation, and vibration but also the complex kinds of atomic motions collectively termed *configurational*, which are governed by strong short-range repulsions and long-range attractions in molecular liquids. The measurement then averages out all these configurations.

Picturing these motions at a microscopic scale is difficult, however, especially for complex liquids or melts with various interacting entities. In various types of glass-forming liquids [5], local order can nonetheless be described in terms of degree of polymerization, formation of channels or sublattices, or formation of interpenetrating networks. Like the advancement of a chemical reaction, such structural features may be described in terms of the aforementioned parameter ξ . In internal thermodynamic equilibrium, i.e. in the liquid state, ξ is equal to $\xi_{eq}(T, P)$, but not in the glass transition range where $\xi(t)$ becomes a function of $T(t)$, $P(t)$, and $A(t)$, revealing its nonequilibrium nature. Below the glass transition range, where the relaxation time of the configurational degrees of freedom exceeds the experimental timescale, they cease to contribute to the measured property. At temperature low enough, the structure then eventually freezes in for good in one state defined by one particular value of $\xi(t)$, which becomes independent of the external parameters T and P .

From a practical standpoint, the timescale defined by the viscosity of the material is important to determine the temperature at which the system will fall out of equilibrium when observed at the timescale of a particular experiment. There is not yet a unique model for describing relaxation phenomena in all glass-forming liquids (Chapter 3.7), whether *strong* or *fragile* with Arrhenian or non-Arrhenian viscosities, respectively [6]. In measurements of macroscopic properties, one nonetheless considers generally that experimental timescales τ_{exp} are of the order of $\tau_{exp} \sim 10^2 - 10^3$ seconds. The viscosity should then be of the order of 10^{12} Pa.s or 10^{13} P for structural relaxation to be complete under these conditions. To stress the usually tremendous variations of

viscosity down to the glass transition, it will suffice to note that the viscosities of stable liquids (i.e. above the melting or liquidus temperature) range from 10^{-3} to 10^2 Pa.s depending on chemical composition and structural type.

4 Glass as a Nonequilibrium Substance

Time-dependent effects appearing at the glass transition are clearly observed in the heat capacities measured for PVAc (Figure 2), which is a model polymeric system extensively studied because of its excellent glass-forming ability and standard T_g close to room temperature. The observed hysteresis loop between cooling and heating demonstrates that the heat capacity does not only depend on T and P but also on time. Moreover, upon heating, the heat capacity shows a typical overshoot, i.e. an endothermic event, named structural recovery process. To come back to the initial liquid state, the system needs to recover the amount of internal enthalpy that has previously been lost. From such measurements, it is possible to determine the configurational contribution to the heat capacity ΔC_p^{conf} . Here, it is defined by the difference at every temperature between the heat capacities actually measured and estimated for the glass phase:

$$\Delta C_p^{\text{conf}} = C_p - C_p^g. \quad (6)$$

This type of definition also applies to other thermodynamic variables such as the thermal expansion coefficient α_p , or the isothermal compressibility κ_T . A configurational contribution consequently represents the thermodynamic contribution that originates in configurational changes in the liquid.

The glassy state then is defined as that for which the configurational movements have been frozen-in, i.e.

$\Delta C_p^{\text{conf}} = 0$. In this state, only the vibrational motions, i.e. the fast degrees of freedom (faster than the experimental timescale), contribute. To define this contribution over the entire temperature interval of interest, an extrapolation of the glass heat capacity from low to high temperatures is needed (Figure 2). The heat capacity of the supercooled liquid can also be extrapolated toward low temperatures (Figure 2). The difference between these values for the supercooled liquid and the glass,

$$\Delta C_p^{\text{conf,eq}} = C_p^l - C_p^g \quad (7)$$

then yields the equilibrium configurational contribution, which keeps increasing below T_g even though the actually observed values do vanish (Figure 3).

From the equilibrium and actual configurational contributions, the variation of the configurational enthalpy ΔH^{conf} and entropy ΔS^{conf} , taken between two temperatures, are calculated with:

$$\begin{aligned} \Delta H^{\text{conf}}(T) &= \int_{T_1}^T \Delta C_p^{\text{conf}} dT \text{ and } \Delta S^{\text{conf}}(T) \\ &= \int_{T_1}^T \frac{\Delta C_p^{\text{conf}}}{T} dT, \end{aligned} \quad (8)$$

where $T_1 = 360$ K is in Figure 2 an arbitrarily selected reference temperature.

Absolute values of both state functions could be obtained from the enthalpy and entropy of an isochemical crystalline compound through the crystallization values of these functions (see Figure 1). For lack of such a compound for PVAc, only relative values are thus presented (Figure 4) in such a way that both the actual and equilibrium values are equal from 360 K to the temperature of about 315 K at which internal equilibrium is lost. Since these variations are similar for the configurational enthalpy and entropy, only the former is shown in Figure 4.

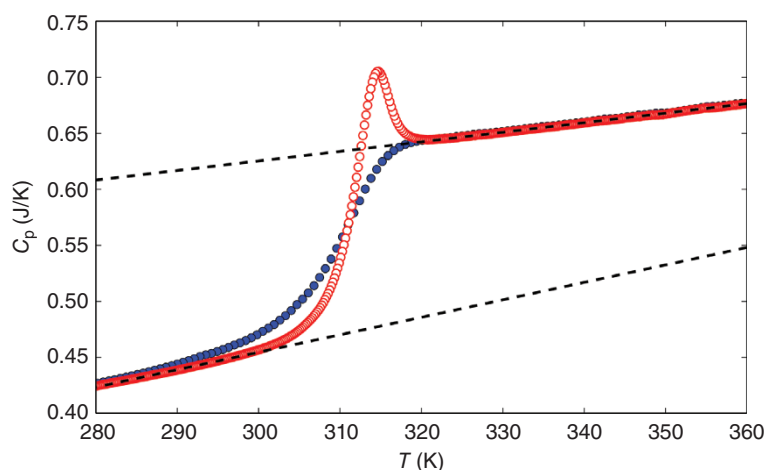


Figure 2 Heat capacity of PVAc measured across the glass transition range by differential scanning calorimetry at the same rate of 1.2 °C/min first upon cooling (solid circle) and then upon heating (empty circle). Dashed lines: fits made from the heat capacities measured for the glass and supercooled liquid.

Figure 3 Configurational heat capacity of PVAc across the glass transition range upon cooling: configurational contribution (solid circle) and equilibrium configurational contribution (empty circle).

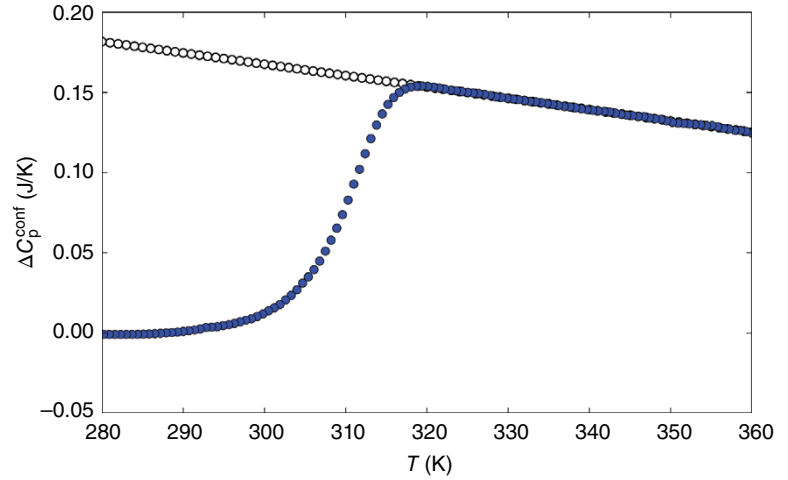
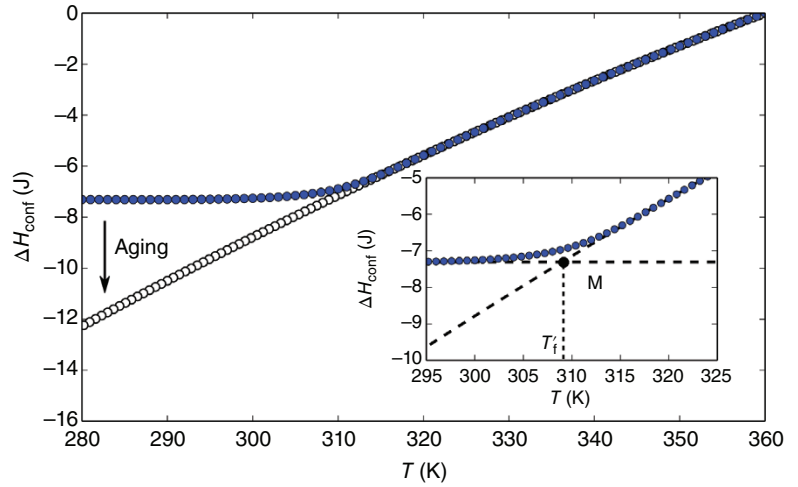


Figure 4 Difference between the configurational enthalpy of PVAc and a zero reference-value taken at 360 K. Actual value (solid circle) and equilibrium value (empty circle). Inset: magnification of Figure 4 showing extrapolated values of the glass and supercooled liquid of this differential configurational enthalpy intersecting at the point M , which defines the limiting fictive temperature $T_M = T_f'$.



Contrary to their equilibrium counterparts, which continue to decrease upon cooling, both the actual configurational enthalpy and configurational entropy level off in the amorphous state (Figure 4). Owing to the large width of the glass transition range, the heat capacity variations at the glass transition are much too smooth to be interpreted as reflecting the discontinuity of a second-order phase transition. Such a discontinuity can nonetheless be identified at a temperature T_M defined by the intersection of the extrapolated glass and supercooled liquid (Figure 4, inset). Both configurational enthalpy and entropy are thus continuous at that temperature, which separates the glass from the supercooled liquid. The same applies to other properties such as volume. Because entropy and volume are the first derivatives of the Gibbs free energy with respect to temperature and pressure, respectively, the following relations initially derived by Ehrenfest should hold when second-order derivatives of the free energy vary discontinuously at this point M :

$$\left. \frac{dP}{dT} \right|_M = \frac{\Delta\alpha_P}{\Delta\kappa_T} \quad (9a)$$

$$\left. \frac{dP}{dT} \right|_M = \frac{\Delta C_P}{T_M V_M \Delta\alpha_P}. \quad (9b)$$

To express these equations in terms of discontinuities of equilibrium configurational contributions at T_M , e.g. $\Delta C_P^{\text{conf,eq}}$ of Eq. (7), Prigogine and Defay [7] assumed that the supercooled liquid is in internal equilibrium down to T_M (i.e. $A = 0$ and $dA = 0$) whereas the glass below T_M is defined by $d\xi = 0$. These two equalities can then be grouped to yield the so-called Prigogine–Defay (PD) ratio [7]:

$$\Pi = \frac{\Delta C_P \Delta\kappa_T}{T_M V_M (\Delta\alpha_P)^2}. \quad (10)$$

Table 2 Thermodynamic parameters measured from five different glass-formers.

Material	T_g (K)	ΔS_0 (J/K/mol)	PD ratio	T_K (K)	T_0 (K)
SiO ₂	1480	5.1	$>10^3$	1150	NA Arrhenius relaxation
CaAl ₂ Si ₂ O ₈	1109	36.2	1.5–22	815	805
Glucose	305	1.7	3.7	241	242
PVAc	301	NA No crystal	2.2	239	250
Glycerol	183	19.4	3.7	134	123
Se	295	3.6	2.4	207	226

The values are taken from the literature.

Although considering an internal parameter ξ , this approach assumes that the glass transition occurs continuously at T_M where $\xi_g = \xi_l$. If so, it would follow from Eq. (9) that the PD ratio should be unity. As indicated by the values listed for widely different glass-forming liquids (Table 2), however, calculated PD ratios are higher or even much higher than unity. One can explain such values by taking into account the kinetic nature of the glass transition [8]. Physically, it is making sense to assume that isobaric temperature derivatives such as ΔC_p or $\Delta \alpha_p$ are not measured under the same kinetic conditions as an isothermal pressure derivative like $\Delta \kappa_T$. Whereas this inconsistency may be removed if more than one internal order parameters ξ are involved in the thermodynamics of the glass transition [9], the problem may in contrast be compounded by the uncertainties arising from the extrapolation procedures used for deriving the relevant parameters at the temperature T_M .

Another puzzling fact has been long ago pointed out by Kauzmann [10] who wondered what would happen if the entropy of a supercooled liquid were extrapolated down to temperatures much lower than the experimentally observed T_g . The conclusion was that it would become lower than that of the isochemical crystal at a temperature T_K , thus termed the Kauzmann temperature (Table 2), which could suggest that the liquid undergoes a continuous phase transition toward the crystalline phase at T_K analogous to the critical point of fluids.

One way out of the paradox implies kinetic arguments and assumes that the viscosity of the supercooled liquid diverges at a temperature close to T_K . This assumption may be represented by the Vogel–Fulcher–Tamman (VFT) equation (Chapter 4.1):

$$\eta = A \exp \left(\frac{B}{T - T_0} \right), \quad (11)$$

where the temperature T_0 of the viscosity divergence is actually close to the Kauzmann temperature (Table 2)

even though they may depend on the specific sample and the method of measurement.

Another way out is to take with great caution the extrapolations of the heat capacity and other thermodynamic functions of the supercooled liquid. As long pointed out [e.g. 11], there is no current theory for these properties in liquid state analogous to the Einstein or Debye models that provide functional forms at all temperatures for heat capacities of crystals.

As derived from strikingly old questions in glass science, these counterintuitive features indicate that glasses cannot be described by equilibrium thermodynamic states only. Nonequilibrium thermodynamics is, therefore, likely to be useful to characterize glasses and the glass transition.

5 Nonequilibrium Thermodynamics of the Glass Transition

The questions raised by the Kauzmann paradox or the PD ratio clearly illustrate the need for a more fundamental thermodynamic description of the glass transition. Following the pioneering work of Tool [12, 13] and Davies and Jones [9], different approaches and phenomenological models have been developed to deal with the glass transition range itself, many within the framework of classical nonequilibrium thermodynamics [4, 11].

The starting point has been the phenomenological concept of fictive temperature (T_f) propounded by Tool [12, 13] to characterize the state of a relaxing system at any time. This temperature is similar to an order parameter ξ . It thus overcomes the limitations of the fixed limiting temperature T_M , which characterizes only the point at which internal equilibrium is suddenly lost in a quenched state. On an analogous basis, a more detailed description is made in terms of two-temperature thermodynamics [14] whereby the vibrational and configurational degrees

of freedom are distinguished by a “classical” temperature for fast modes (phonons bath), and an effective temperature for the slow modes, respectively.

The first physical models have then relied on two different approaches. In free-volume theories, one generally considers that the dynamics of the system is determined by the free space present around its atoms, which makes configurational rearrangements more or less easy. In entropy theories, among which that of Adam-Gibbs is the best known [15], the same determining role is attributed to configurational entropy. In other words, these theories assign the strong increase of relaxation times with decreasing temperatures and the eventual structural freezing in to decreases of either free volume or configurational entropy. Other more recent theories of the glass transition rely on mode coupling, random first-order transitions or energy-landscape descriptions [e.g. 16]. These different approaches have the common goal of finding the exact expression for the structural relaxation time, or its distribution, as a function of controlling parameters such as temperature or pressure, or structural order parameter.

For the sake of simplicity, let us consider here conditions of constant pressure. If the additional parameter ξ is taken into account, the total differential of the enthalpy of a system can be written as the sum of two contributions (considering pressure, the generalization to three contributions would be obvious):

$$(dH)_P = \left(\frac{\partial H}{\partial T}\right)_{P,\xi} dT + \left(\frac{\partial H}{\partial \xi}\right)_{P,T} d\xi. \quad (12)$$

The isobaric heat capacity is written as:

$$C_P = \left(\frac{dH}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_{P,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{P,T} \left(\frac{d\xi}{dT}\right)_P. \quad (13)$$

The first term on the right-hand side is the heat capacity at constant ξ , i.e. C_P^{glass} , and the second, the configurational contribution ΔC_P^{conf} as defined by Eq. (6). To account for the kinetic nature of the glass transition, it is then necessary to rewrite Eq. (13) as:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{P,T} \left(\frac{d\xi/dt}{dT/dt}\right)_P. \quad (14)$$

When the rate of change of ξ becomes much smaller than the rate of change of temperature, $(d\xi/dt)_P \ll (dT/dt)_P$, the configurational contribution is negligible.

Hence, it is the ratio between these two rates that is controlling the relative value of the experimentally recorded configurational heat capacity. This ratio is maximum in the supercooled liquid state, and decreases throughout the glass transition range to become

negligible in the glassy state (cf. Figure 3). There, only the first right-hand side term in Eq. (14) contributes:

$$\begin{aligned} C_{P,\xi} &= C_P^{\text{glass}} < C_P < C_P^{\text{eq}} \\ &= C_P^{\text{liquid}} \text{ or } 0 < \Delta C_P^{\text{conf}} < \Delta C_P^{\text{conf,eq}}. \end{aligned} \quad (15)$$

The next step thus consists in taking into account the time dependence of ξ at every temperature through the temperature dependence of the relaxation time τ . The simplest way to do this is to assume a simple exponential decay for ξ at fixed temperature and pressure:

$$\frac{d\xi}{dt} = -\frac{(\xi - \xi_{\text{eq}})}{\tau}, \quad (16)$$

where $\xi_{\text{eq}}(P, T)$ is the equilibrium value of the order parameter, i.e. a variable characterizing the liquid structure that depends only on P and T . Although the relaxation time itself has been given different temperature dependences with Arrhenius, VFT, or others laws (Chapter 3.7), the important point is that they are all of an exponential nature with respect to T or P to ensure the structural freezing-in of the system.

Interesting applications of these concepts have been made with the lattice-hole model of liquids, which has the advantage of lending itself to an evaluation of the order parameter ξ . Schematically, this model considers a liquid as a lattice in which disorder is represented by unoccupied sites whose fraction x depends on both temperature and pressure [17]. From the equilibrium value of the order parameter, it is thus possible to solve the linear differential Eq. (16) to find its temperature dependence and, then, to calculate the variations of the heat capacity within the glass transition range under varied conditions [18]. Likewise, the configurational Gibbs free energy may also be computed analytically as a function of temperature, pressure, and order parameter. A similar approach has been followed to incorporate the effects of pressure in the expression of the structural relaxation time for determining also how the heat capacity, thermal expansion coefficient, and isothermal compressibility vary under different conditions [19].

From the configurational Gibbs free energy calculated for the lattice-hole model, one readily simulates with the definition (3) of the affinity its variations upon vitrification (cooling) and structural recovery (heating) [19]. Thermodynamic data measured on *o*-terphenyl may be used to simulate the corresponding affinities during temperature ramps (Figure 5): cooling at 0.3 K/min from an initial temperature of 255 K is followed by heating at the same rate, and then by further cooling at 0.5 K/min preceding final heating at 20 K/min. That the supercooled liquid begins to lose internal equilibrium from 248 K is indicated by the departure at this temperature of the affinity curve from the zero line, which represents the

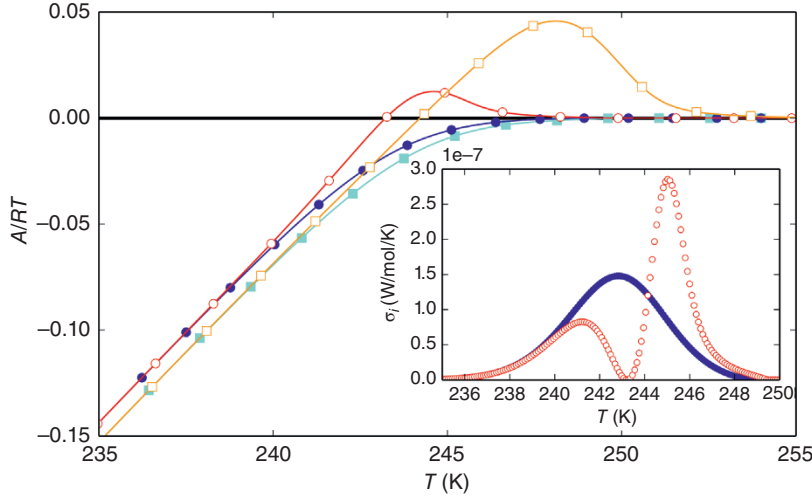


Figure 5 Simulated affinities of *o*-terphenyl in the glass transition range upon cooling and heating as calculated from the lattice-hole model. Solid circle for -0.3 K/min and solid square for -0.5 K/min; empty circle for $+0.3$ K/min and empty square for $+20$ K/min. The horizontal line represents equilibrium ($A = 0$). Inset: entropy production rates calculated from the previous affinities. Solid circle upon cooling and empty circle upon heating.

maximum (equilibrium) value of the affinity during cooling. The affinity then linearly decreases with temperature below 240 K in the glassy state, with higher values for slower cooling as a result of lower glass transition temperatures. Upon heating, the affinity begins to increase linearly according to the same line pathway before crossing the equilibrium line. It then exhibits a peak whose position shifts toward higher temperatures and whose magnitude and width increase with the heating rate in ways such that the configurational heat capacity and the other thermodynamic coefficients can be simulated [19].

The entropy production can also be calculated from Eq. (4) (inset in Figure 5). In agreement with previous results [18], it shows a single peak upon cooling but two peaks upon heating. With respect to the experimental data, the advantage of the calculation is thus to distinguish clearly two contributions to the entropy produced when heat is brought to the material. The first peak is associated with a decrease of the configurational energy of the system, which is taking place because of the delay introduced by the relaxation time, even though heat is being supplied. As to the second peak, it is in contrast associated with the configurational energy necessary to recover internal equilibrium in the supercooled liquid state.

Here the wording “is associated” instead of “represents” is necessary because the entropy produced and configurational entropy changes necessarily differ as a result of the irreversible nature of the glass transition. Whereas the entropy production is the product of the thermodynamic force and flux (see Eq. (4)), the variation of the configurational entropy is written as, see Eqs. (8) and (13):

$$\frac{dS^{\text{conf}}}{dt} = \frac{\Delta C_p^{\text{conf}}}{T} \times \frac{dT}{dt} = \frac{(\partial H / \partial \xi)_{p,T} (d\xi/dt)_p}{T}. \quad (17)$$

The rate of entropy production thus reflects the spontaneous or irreversible microscopic processes that take place within the system during relaxation. As dictated by the Second Law of thermodynamics, it is always positive whether upon cooling or heating (Figure 5, inset). Physically, it can be thought of the heat irreversibly generated by friction at a microscopic scale. The resulting thermal power $P_i = T\sigma_i$, where σ_i is the entropy creation in Eq. (4), is produced much too quickly to be compensated instantaneously by an exchange of heat with the surrounding heat bath. Under this circumstance, this is why an effective or fictive temperature can be defined. This surrounding heat bath is sometimes called the phonon bath since it is characterized by fast or vibrational modes.

On the contrary, the change in configurational entropy is a reversible process related to the heat exchanged with the surrounding heat bath whose relevant thermal power is:

$$P_{\text{th}} = T \frac{dS^{\text{conf}}}{dt} = \Delta C_p^{\text{conf}} \times \frac{dT}{dt}. \quad (18)$$

Because the configurational entropy becomes constant upon vitrification, its variations have vanished (i.e. the configurational heat capacity) below the glass transition range. Above this range, in the supercooled liquid state, they of course differ from zero as indicated by

$$\begin{aligned} \frac{dS^{\text{conf,eq}}}{dt} &= \frac{\Delta C_p^{\text{eq}}}{T} \times \frac{dT}{dt} \\ &= \frac{(\partial H / \partial \xi)_{p,T}^{\text{eq}} (d\xi_{\text{eq}}/dT)}{T} \times \frac{dT}{dt}. \end{aligned} \quad (19)$$

In the transition range, the variations of the configurational entropy of the system are consequently positive or negative upon heating and cooling, respectively. As

already evaluated long ago either theoretically [9] or experimentally [20, 21], the entropy produced is generally negligible with respect to the configurational entropy changes. The integration of the heat capacity curves measured by calorimetry is thus a pertinent way to access to the absolute value of the residual entropy at 0 K [3]. As seen from a direct comparison of Eqs. (4) and (17), arriving at this conclusion is tantamount to neglecting the affinity with respect to the enthalpy of advancement of the configurational change at every temperature:

$$\text{Entropy production negligible} \iff A \ll \left(\frac{\partial H}{\partial \xi} \right)_{P,T} \quad (20)$$

6 Physical Aging

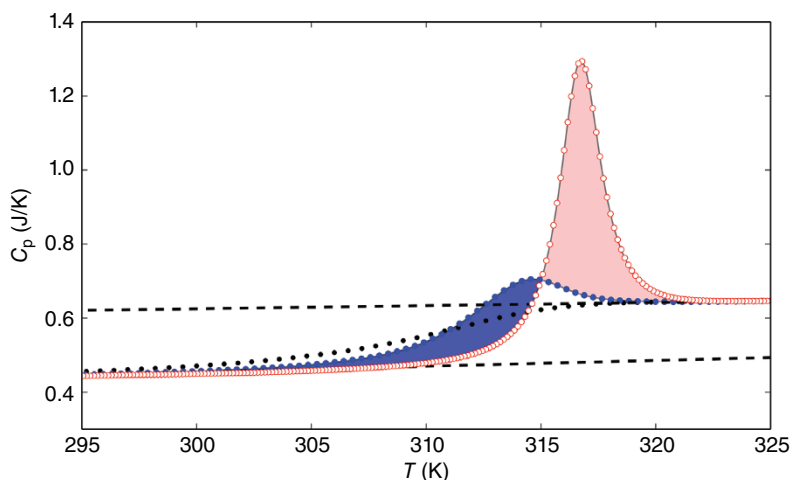
Relaxation times that depend only on temperature and pressure have been considered. Nevertheless, the complexity of microscopic structures in glasses implies the existence of a distribution of relaxation times. Relaxation processes then also depend on the instantaneous state of the system itself and, thus, on its history as, for instance, described by the Tool–Narayanaswamy–Moynihan model (Chapter 3.7, [22, 23]). A consequence is that some non-trivial relaxation processes can take place well below the glass transition range. Hence, it is interesting to study such a time-dependent process termed *physical aging*, which has a practical relevance through its possible effects on glass properties.

The process can be illustrated with DSC scans for PVAc (Figures 2 and 6). If the sample is cooled down at some rate to 297 K, i.e. about 10 K below the calorimetric T_g , and its temperature is kept constant for a time interval t_a , then its enthalpy (and entropy) relax to their lowest equilibrium values for the temperature (and pressure)

considered. Experimentally, physical aging manifests itself as differences between the areas of DSC scans upon heating recorded for samples annealed (72 hours at 297 K) and not annealed. For the experiment without annealing, the lowest temperature of 278 K has been directly reached (see cooling curve in Figure 6). The amount of enthalpy relaxed during aging is equal to the difference between the light gray and dark gray areas in Figure 6. Of course, for a given annealing temperature, such a difference increases with the aging duration. As recently carried out on polymeric glass-formers annealed at relatively low aging temperatures for a very long time, calorimetry (DSC) can bring to light two different timescales for glass equilibration, revealing the complexity and richness of relaxation processes well below T_g [24].

Phenomenologically, however, in simple cases aging can be accounted for with the same approach as developed in previous sections. It is related to the relaxation of the order parameter ξ toward its equilibrium value $\xi_{eq}(P, T)$ whereas the affinity A is relaxing at the same time toward zero. When applicable, the lattice-hole theory can be used to solve Eq. (16) at constant P and T to reproduce the observed process. As done for *o*-terphenyl [19], the order parameter is calculated at constant pressure and aging temperature $T = 229.5$ K with Eq. (16) and a temperature- and pressure-dependent relaxation time [19]. The affinity has been calculated upon heating at 60 K/min, either after cooling at 6 K/min without aging, or after cooling at the same rate but with an aging process at 229.5 K (Figure 7). Upon isothermal aging, the affinity increases markedly (see the arrow in Figure 6) and then increases at the same rate as without aging. The difference is that the zero line is crossed at a lower temperature so that a much bigger peak is observed when the affinity finally recovers its zero equilibrium value at high temperatures. Since the affinity is an integrated measure of the heat capacity, the large peaks either calculated or

Figure 6 Effect of aging on the heat capacities of PVAc recorded upon heating at the same rate. Heat capacity after a cooling (solid circle with line) and heat capacity after cooling and 72-hour annealing at 297 K (empty circle with line). The enthalpy released during aging estimated by the difference between the two areas included between these two curves. Heat capacities upon continuous cooling shown as solid circles.



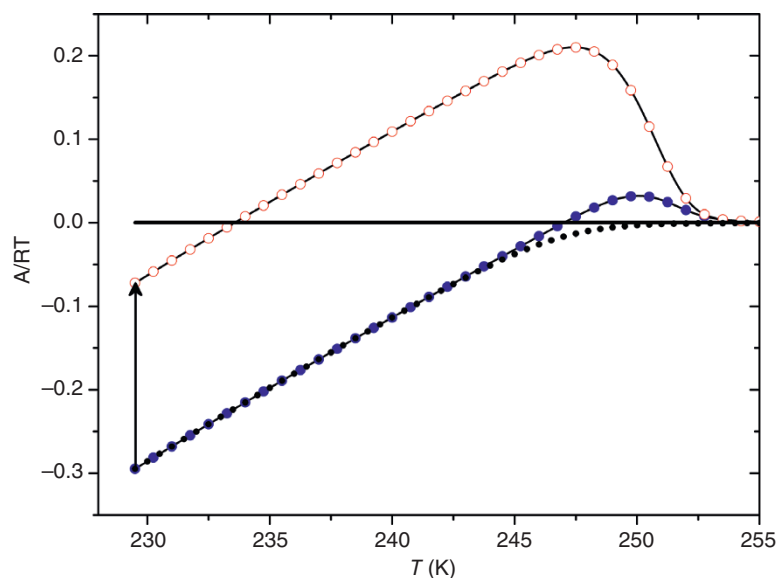


Figure 7 Effect of aging on affinities calculated with the lattice-hole model upon heating at the same rate of 60 K/min, first after a continuous cooling at 6 K/min (black line with solid circle), and second after annealing at 229.5 K (black line with empty circle). The black arrow simulating the relaxation of affinity upon aging at 229.5 K. Affinity upon continuous cooling shown as solid circles.

observed for these properties are clear signatures of aging [19]. More complex calculations can of course be made to deal with at least two separate timescales [24], or a more realistic distribution of relaxation times.

7 Perspectives

Whether in the form of affinity, fictive temperature, or structural order parameter, additional variables must be introduced to deal with the nonequilibrium thermodynamics of glass-forming systems and, in particular, with the time dependence of their properties in relaxation regimes. Phenomenological advances now make it possible to predict these properties as a function of time and temperature or to determine accurately the entropy irreversibly produced, but the mechanisms involved at the atomic or molecular level generally remain to be deciphered. The physical nature of the glass transition is a case in point, as are the origins of Kauzmann catastrophe, of the strong variations of the PD ratio, of the diversity of relaxation timescales or of, as illustrated by the well-known memory effects, the complex nonlinear coupling of the parameters of the differential equations with which these processes are described.

Not only could highly sensitive calorimetric experiments yield valuable original data in this respect but coupling of different techniques such as dielectric spectroscopy and temperature-modulated calorimetry should bring new insights on the dynamics and thermodynamics of the glass transition. Recent experiments on ultra-stable organic glasses obtained by vapor

deposition techniques are, for instance, promising [25, 26]. And whereas very long aging performed well below T_g should also give new clues on the laws driving complex relaxation processes in the glassy state [24], experiments made at extremely rapid timescales (e.g. spectroscopy) are in contrast needed to investigate relaxation in supercooled liquids where equilibrium is quickly achieved. To give a single example, ultrastable organic glasses obtained by vacuum-deposition techniques should be of special interest in view of their internal stability that is equivalent of that of hyper-aged glasses (with aging time of millions of years) obtained by conventional melt cooling [25]. For this particular class of glasses, the aforedefined T_M values are so much lower (by a few tens of degrees) than the standard glass transition temperatures that T_M and T_g cannot be indiscriminately used in Eq. (9b) [25, 26]. Among other consequences, new insights should then be gained on the non-unity of the PD ratio. Finally, such experiments should of course be firmly complemented by fundamental work. Microscopic theories and atomistic simulations must be developed and, as stringent tests of their value, their predictions checked in terms of macroscopic physical properties.

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3.3

The Glass Transition and the Entropy Crisis

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1 Introduction

Vitrification [1–3] is a prime example of an irreversible process going on at low temperatures T_0 or high pressures P_0 of the surrounding medium (which may be different from those of the system of interest). It is commonly believed now that almost all materials including organic and inorganic substances, man-made polymers, metals, plastics, biomaterials, drugs, etc., can be turned into a glass (or vitrified) with a suitable technique (Table 1). But our understanding of the glassy state (GS) is far from complete, mainly because they exhibit a *duality* in their properties, appearing either liquid- or solid-like at long or short timescales, respectively [2]. Molecular motions in liquids become progressively slower as vitrification is approached, with a characteristic time increasing from nanoseconds to beyond feasible experimental timescales time τ_{exp} (the inverse of the probed frequency ω) of the order of 10^2 to 10^5 seconds, i.e. one day (Chapter 3.7). This results in an operational definition of a range of temperatures T_{og} -to- T_{OG} for the glass transition (GT). Following convention, however, we simply use T_{og} as the transition temperature to specify this range, which is determined by the rate of approach to the transition.

The slow glassy dynamics is thought to occur because particles form cooperative groups of increasing sizes, which then define a *correlated length* as the ratio $\zeta_0 \equiv P_0/T_0$ increases. This is the idea behind the celebrated Adam–Gibbs theory [7] of the GT. A similar time dependence is also found in spin glasses, which exhibit an exponentially large number of metastable states below

the (spin-)GT temperature due to the presence of *frustration*, namely, the inability of the system to minimize simultaneously the (sometimes competing) interaction energies between its constituents. This similarity has suggested frustration to be also important for a regular glass [8], although the situation is not very clear.

There are many excellent recent monograph and reviews [3, 8–10] on glasses, from which the present chapter differs by its emphasis on nonequilibrium thermodynamics and its attempt to identify the communal entropy and the free volume to provide a thermodynamic unified approach to glasses [11]. We do not specifically discuss the actual form of the temporal variation except to note that the most common empirical law, valid in a limited domain, is the Kohlrausch stretched exponential $q(T_0, t) = q_0 \exp(-t/\tau)^\beta$ [8, 9], where the property q and some average *relaxation time* τ must be state-dependent quantities. In the next section, we review some important concepts and theories. It is followed by a description of glassy phenomenology in Section 3. Nonequilibrium thermodynamics used here is briefly introduced in Section 4, and its consequences for glassy relaxation are considered in Section 5. The topics of free volume and the communal entropy are taken up in Section 6. We follow this by a resulting unifying approach in Section 7. The final section contains a discussion of the results and the limitation of the approach. The present chapter partially complements the previous one.

2 Important Concepts and Theories

2.1 Fast and Slow Modes

There is a hierarchy of relaxation modes [11] in a glass. Phenomenologically and for the sake of simplicity, however, we can broadly speaking divide them into at least

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Table 1 Transition temperatures of some materials.

Material	T_{0g} (K)	T_{0K} (K)	Material	T_{0g} (K)	T_{0K} (K)	Ref.
1-Butene	58	48	Salol	220	167	[4]
Toluene	126	96	Glucose	306	271	[4]
Selenium	307	240 ± 10	$ZnCl_2$	380	250 ± 25	[4]
Glycerol	193	135	$H_2SO_4 \cdot 4 H_2O$	157	133	[4]
Diopside	1005	637	Anorthite	1160	815	[5, 6]

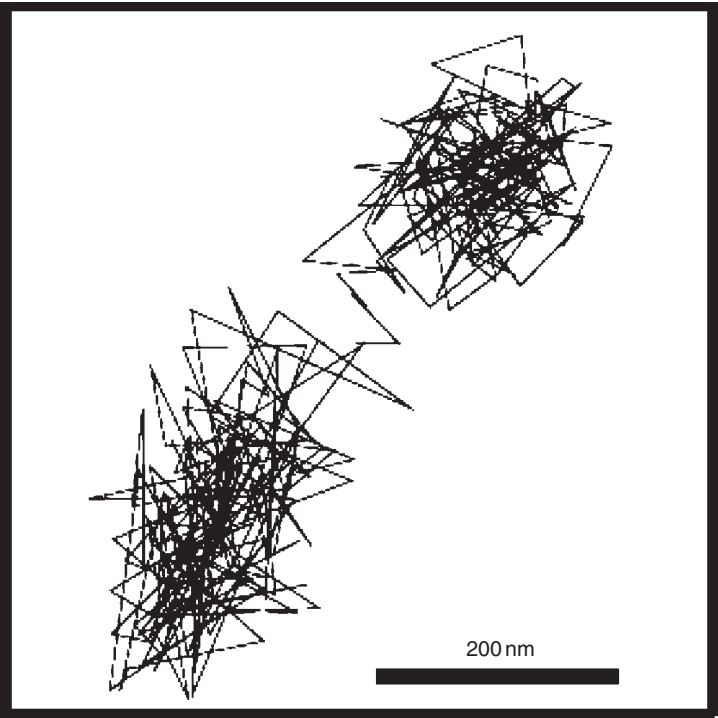


Figure 1 The 2-D projection of a typical 3-D trajectory for 100 min for $\phi = 0.56$. Most of the time, particles are confined to their cages. Occasionally, a particle will move a long distance and get trapped in another cage. In the figure, the particle took 500 seconds to shift its position. Source: Reprinted with permission from [12].

two distinct and widely separated timescales governing fast and slow modes in glasses. The former refers to the localized oscillations of the particles (atoms, molecules, segments, monomers, etc.) in the cells or cages formed by neighboring particles, and the latter to the translation and diffusion (translation over long distances [1]) of particles. In Figure 1, we show a two-dimensional projection of a three-dimension trajectory of a colloidal particle at high enough density, which oscillates within its cage for a long time before leaving to a new cage in which it oscillates again to leave it later on, and so on. These two distinct modes distinguish the glass from other nonequilibrium states where there is only one mode to be considered. Owing to its complexity, and its incomplete and sometimes controversial understanding, vitrification continues to attract researchers to this date.

2.2 What Is a Glass?

As a physicist, we first need to ask is: What is a glass? The simple and most common answer is that glass or GS is a time-dependent nonequilibrium state of matter [2, 3, 13] found at low temperatures T_0 and/or high pressures P_0 of the surrounding medium. It undergoes GT from a relatively brittle solid glass into a molten state (the super-cooled liquid [SCL]) as ζ_0 decreases. The striking feature of a glass, which distinguishes it from an equilibrium crystal (CR), is that it has much higher potential energies [14]. Even at absolute zero, there remains a non-zero gap between their energies. Thus, a glass can be thought of as a macrostate which has trapped a lot of frozen defects relative to the crystal that were present in the equilibrium liquid (EL) at the melting point [15]. Glass is

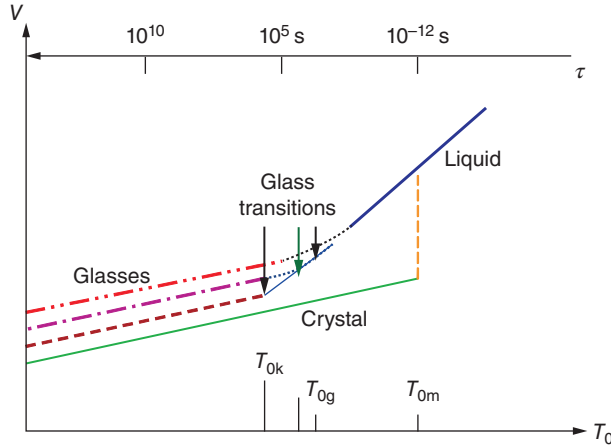


Figure 2 Schematic variation of the volume as the liquid is cooled. The freezing transition from the equilibrium liquid (line above T_{0m}) to the crystal (shown by the green line) occurs at T_{0m} ; the latter becomes perfectly ordered at absolute zero. Bypassing crystallization leads to the supercooled liquid (shown by the line as the continuation of the equilibrium liquid). The supercooled liquid bends continuously without any discontinuity in the slope into different glasses (shown by different broken lines) at different glass transition temperatures (T_{0g}) depending on the rate of cooling r . As r decreases, T_{0g} also decreases (shown by arrows becoming larger), until finally it converges to its limit T_{0k} under infinitely slow cooling rate ($r \rightarrow 0$) but now with a discontinuity in the slope. This limit is called the *ideal glass transition temperature* or the *Kauzmann temperature*, and the corresponding glass shown by the dashed curve is time-independent and is called the *ideal glass* (IG). A similar variation of the slopes of the density is also seen when we increase P_0 at a fixed T_0 ; we merely replace T_0 in the figure by $1/P_0$. Thus, we can replace the horizontal axis by $1/\zeta_0$.

most commonly prepared in the laboratory by cooling or compressing the SCL to fall out of equilibrium (Figure 2). The genuine equilibrium state corresponds to the crystal. This does not mean that the SCL can never be treated as in equilibrium; its stationary limit, called the equilibrium supercooled liquid (ESCL) with a stretch of imagination, can be treated as an equilibrium state under the restriction that only *disordered* microstates are considered [15], a sensible restriction to study glasses. The simplest way to identify these microstates is to introduce an order parameter ρ . It is defined so that $\rho = 0$ for disordered states and $\rho \neq 0$ for ordered states [15]. We denote the restricted space of disordered microstates by $\mathcal{D}$, and refer to the restriction as a *restricted ensemble* formalism in this work to distinguish it from an *unrestricted* ensemble in which *all* microstates are considered. To make a clear distinction, all possible time-dependent SCL states will be called nonequilibrium supercooled liquid (NESCL) states; they occur near but below the bends and are shown as dotted curves, whereas the continuous line refers to the ESCL. In the following, we will use the SCL to refer to both nonequilibrium and equilibrium SCLs. The GS

shown by a broken line is always treated as out of equilibrium and exists way below the bend.

The standard formulation of entropy

$$S(t) = - \sum_k p_k \ln p_k \geq 0 \quad (1)$$

in terms of microstate probability p_k of the *allowed* k th microstate is applicable to any (equilibrium or nonequilibrium) state in both ensembles [16]; p_k depends on the extensive observables (the energy E , volume V , number of particles N , etc.) in addition to the time t . In the stationary limit so that p_k has no t -dependence, these entropies achieve their unique maximum value S_{ESCL} or S_{IG} (S_{CR}) in the restricted (unrestricted) ensemble below T_{0M} . Above T_{0M} , they yield S_{EL} in both ensembles, as expected. In the stationary limit, the entropy is related to the number of microstates W in both ensembles by the famous Boltzmann formula $S = \ln W$ (we set the Boltzmann constant $k_B = 1$ so that the entropy becomes dimensionless).

2.3 Adam–Gibbs Theory

The excess entropy defined as

$$S_{\text{SCL}}(T_0, t) \equiv S_{\text{CR}}(T_0) + S_{\text{ex}}(T_0, t), T_0 < T_{0M} \quad (2)$$

has played a very pivotal role in the field of GT. Kauzmann [13] proved that it exhibits a rapid drop below T_{0M} by for many systems. A smooth *extrapolation* to lower temperatures shows that it eventually vanishes at some temperature below T_{0M} , and becomes *negative* if *extrapolated* to lower temperatures. A (kinetic) transition, i.e. a GT takes place at a higher temperature T_{0g} to avoid this *entropy crisis*, known commonly as the *Kauzmann paradox*. In the limit of zero cooling rate r (not accessible in experiments or simulations, but accessible in a theoretical setup), the GT occurs in the ESCL at $T_0 = T_{0\text{ex}}$ [$S_{\text{ex}}^{\text{ESCL}}(T_{0\text{ex}}) = 0$], see Figure 2, and is known as the *ideal glass transition* (IGT) from the ESCL liquid to an ideal glass below $T_{0\text{ex}}$. It should be stressed, however, that there is no thermodynamic requirement for $S_{\text{ex}}(T_0)$ to be non-negative. There are physical systems like He^4 in which $S_{\text{ex}}(T_0)$ can become negative at low temperatures. This means that the vanishing of $S_{\text{ex}}(T_0)$ *cannot* be an argument for a GT but the vanishing of the communal entropy $S_{\text{ESCL}}^{\text{comm}}(T_0)$, to be defined later, will be as we will discuss.

The thermodynamic theory due to Adam and Gibbs [3, 7–10, 15, 17] attempts to provide a justification of the *entropy crisis* in the ESCL by specifically considering the configurational entropy $S^{\text{conf}}(t) \doteq S(t) - S^{\text{kin}}(t)$ among the positions and interactions (which we take to be independent of momenta) among the particles [15]. Here, $S^{\text{kin}}(t)$ is entropy originating from the kinetic energy of the particles and its separation from $S(t)$ is possible

because the internal energy E can be partitioned into two *independent* contributions from the positions (configurations) and momenta (kinetic energy) of the particles, respectively. In a lattice model such as in the Gibbs–DiMarzio theory [18], $S^{\text{conf}} = S(t)$ as there is no kinetic energy. We must be careful not to confuse $S^{\text{conf}}(T_0, t)$ with $S_{\text{SCL}}(T_0, t)$ as they are different quantities. The central idea in the Adam–Gibbs theory is that the sluggishness observed in a system is a manifestation of the smallness of the configurational entropy, i.e. the smallness of the available configurations to the system. From this theory, it follows that the viscosity $\eta(T_0)$ above the GT is given as follows:

$$\ln \eta(T_0) = A_{\text{AG}} + B_{\text{AG}}/T_0 s^{\text{conf}}, \quad (3)$$

where A_{AG} and B_{AG} are system-dependent constants and $s^{\text{conf}} = S^{\text{conf}}/N$. It is commonly believed that the configurational entropy also vanishes at a positive temperature $T_{0\text{S}}$ (where $\eta(T_{0\text{S}})$ diverges), which is not identical to $T_{0\text{ex}}$, although they are close [17]. The derivation of Eq. (3) is based on the concept of cooperative domains of size z , which gradually increases as the temperature is lowered and diverges at $T_{0\text{S}}$. At this temperature, the entire system acts like a cooperative domain. While this particular domain is disordered, its configurational entropy must vanish in this theory. As the laboratory GT temperature $T_{0\text{g}}$ occurs at about 50 K above $T_{0\text{S}}$, the value of z at $T_{0\text{g}}$ is much smaller; it is of the order of 5–10.

2.4 Free Volume Theory

The cell theory of liquids is very appealing to study the motion of individual particles [1, 3] during a GT. The localized oscillatory motion of a particle occurs around the minimum of the potential ϕ generated by its neighbors in the cell. (The set of minima from all the cells determines what is nowadays called the *inherent structure* [3].) Such a motion occurs at all times in the crystal unless there are interstitial vacancies. In a glass, such a motion occurs at short time and endows a glass with solid-like properties (Figure 1). But at long times, there occurs uninhibited translation and diffusion, superimposed on the oscillatory motion controlled by a continuously changing ϕ as the neighbors change [1]. This gives a glass a liquid-like property, whose central feature is the mobility of the particle.

At high densities, the neighbors impede the motion in almost all directions and the motion becomes confined within the cell with little or no diffusion. At low densities, the particle can move almost freely in any direction and diffusion occurs. (The presence of chemical bonding requires the whole molecule to move together and must be eventually accounted for.) As we are interested in the

dense phase, we have both motions possible at different timescales. The ability to move long distances requires what is vaguely termed the *free volume* V_f , and which is *communally* shared by many particles. It gives rise to the *fluidity*. The potential ϕ felt by the particle in its cell endows the particle with what can be termed the *interaction volume* v_i per particle: it is the volume necessary to execute its oscillatory motion in ϕ ; the latter must gradually become very steep as the particle gets close to the neighbors. At low temperatures, these steep portions have almost no chance to be explored by the particle. Therefore, the interaction volume v_i must be usually smaller than the cell volume Δ . Their difference $\Delta - v_i$ gives the particle some elbow room for translation and must be included in V_f . The determination of $V_i \equiv Nv_i$ is somewhat technical and will be discussed later. In terms of the interaction volume V_i , we have

$$V = V_i + V_f; \quad (4)$$

both components are functions of state variables.

Many workers use the concept of occupied volume $V_o \equiv Nv_o$ to define $V_f = V - V_o$. However, the concept may be ambiguous [19]. For some, v_o is just the van der Waals volume, also known as the molecular volume v_m . It is just a parameter of the liquid. In contrast, the interaction volume is theoretically well defined in our approach. To inquire if they are the same is meaningless. As a van der Waals volume is merely a parameter, V_o is just a constant equal to Nv_m . Such a definition will not account for the sudden change in the temperature variation (the slope) of the ideal glass volume at the kink in Figure 2. Our definition of V_i allows for such a variation.

The free volume theory of Doolittle [17, 20] has attempted to describe the GT with some respectable success even though lately it has fallen out of favor. This is unfortunate as it captures the essence of the GT, which then occurs when the free volume becomes sufficiently *small* to impede the *mobility* of the molecules [20]. The Doolittle equation correctly predicts the abrupt increase in the viscosity for a large number of glass formers in a narrow range over which v_f becomes very small [17]. According to this equation, the fluidity ϕ , which is basically the inverse of the viscosity η , is given by

$$\phi \equiv \eta^{-1} = \phi_0 \exp(-\gamma v_m/v_f), \quad (5)$$

where γ is a fitting parameter of order unity. Phenomenologically, we identify a GT to occur normally when $\eta \gtrsim 10^{13}$ poise or $\tau \simeq \tau_{\text{exp}}$; see the upper axis in Figure 2. In the Doolittle equation, the parameters γ and v_m are *constant*. But in general, these parameters must be functions of the state variables. With this dependence, we will refer to the above equation as the *generalized Doolittle equation*. The free-volume picture provides a very nice way to think of the GT [1] with percolation of the free volume

as an important ingredient [17]. The time dependence of the free volume redistribution, determined by the energy barriers encountered during it, should provide a *kinetic* view of the transition, and must be properly accounted for. This approach is yet to be completed to satisfaction. One finds that a linear temperature-dependent $v_f = a(T_0 - T_{0V})$, $T_{0V} \neq 0$, a and T_{0V} constants, is satisfied only over a narrow range of the temperature T_0 for most substances [17]. Assuming the linear dependence, we find that $\eta(T_0)$ diverges near T_{0V} according to the phenomenological Vogel–Tammann–Fulcher equation

$$\ln \eta(T_0) = A_{VTF} + B_{VTF}/(T_0 - T_{0V}), \quad (6)$$

where A_{VTF} and B_{VTF} are system-dependent constants (Chapter 4.1). At T_{0V} , V_f vanishes so that there cannot be any translational motion, i.e. any flow, which is consistent with a diverging $\eta(T_{0V})$. The system becomes completely *jammed* [8]. The entropy associated with the translational motion, which we call the *communal entropy* S^{comm} , must also vanish (Section 6.2). The temperature where $S^{\text{comm}} = 0$ will be denoted by T_{0K} in this chapter, and our attempt is to define V_f such that $T_{0V} = T_{0K}$.

The vanishing of V_f is reflected in the variation of the volume; see the point on the lowest curve at temperature T_{0K} in Figure 2, where there is a sharp kink and a discontinuity in the slope. (We have identified the temperature as T_{0K} rather than T_{0V} with the anticipated result obtained later that the Kauzmann temperature T_{0K} , where the communal entropy vanishes, is the same as T_{0V} . This is, as it should be, because the ideal glass shown by the dashed line must be a *unique* state.) This curve is the result of extrapolation $r \rightarrow 0$ to obtain the ESCL (solid curve) and the ideal glass (dashed curve); as a result, there is a singularity at T_{0K} . The presence of free volume above T_{0K} gives rise to different expansion coefficients on the two sides of T_{0K} (Figure 3b). In contrast, the communal entropy does not vanish in Figure 3a so there is no IGT at a positive temperature in this case. The free volume and S^{comm} do not vanish for the laboratory glasses shown by the upper two curves in Figure 2.

Similar to the Kauzmann temperature T_{0K} for isobaric vitrification at fixed P_0 , a Kauzmann pressure P_{0K} can also be identified in the ESCL where $S_{\text{ESCL}}^{\text{comm}}(P_0) = 0$ as the pressure is increased at fixed T_0 . We will collectively call them Kauzmann points.

2.5 Random First-Order Theory

An alternative thermodynamic theory for the impending entropy crisis based on spin-glass ideas has also been developed in which proximity to an underlying first-order transition is used to explain the GT [10]. The theory is

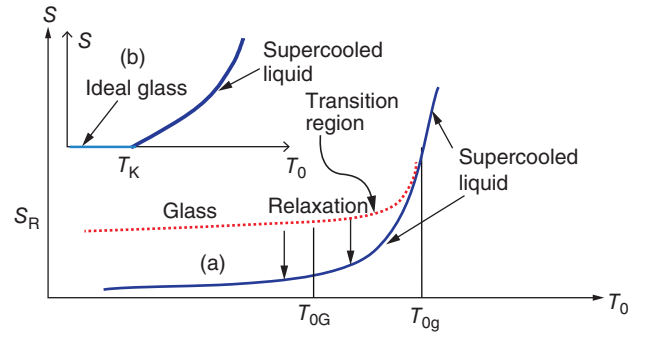


Figure 3 Schematic variation of the communal entropy S^{comm} (a) of the equilibrium supercooled liquid (solid curve) and a possible time-dependent supercooled liquid, which turns into a glass (dotted curve) during vitrification. It is assumed that there is no ideal glass transition in the equilibrium supercooled liquid. The transition region between T_{0g} and T_{0G} has been exaggerated to highlight the point that the glass transition is not a sharp point. For all temperatures $T_0 < T_{0g}$, the nonequilibrium supercooled liquid undergoes isothermal (fixed temperature T_0) structural relaxation in time toward the equilibrium supercooled liquid. The entropy of the equilibrium supercooled liquid is shown to extrapolate to zero, but that of the glass to a nonzero value $S_R > 0$ at absolute zero. (b) S^{comm} of the equilibrium supercooled liquid for a system with an ideal glass transition at T_{0K} , below which we obtain the ideal glass for the equilibrium supercooled liquid. In the restricted ensemble, S^{comm} for the equilibrium supercooled liquid becomes negative below T_{0K} . We conjecture that for all glass-forming systems, the correct form of S^{comm} for the equilibrium supercooled liquid in (a) is the one shown in (b) with an ideal glass transition.

based on the one-step replica symmetry breaking in spin glasses. The one-step replica symmetry breaking is identified in a long-range spin glass model so the theory is at a mean field level. Whereas some may consider this to be a weakness of the theory, it also provides a new level of intuition about ordinary glasses.

2.6 Mode-Coupling Theory

The mode-coupling theory [8] is an example of theories based on kinetic ideas, which deals not with the GT but with the transition at the mode-coupling temperature $T_{MC} > T_g$. Thus, it is not directly relevant for our review. This theory may be regarded as a theory based on first-principle approach, which starts from the static structure factor. In this theory, the ergodicity is lost completely, and structural arrest occurs at T_{MC} .

3 Nonsingular Glass Phenomenology

3.1 The Restricted Ensemble

As is well known, singularity at a phase transition emerges as the system makes a transition between two *distinct* equilibrium phases such as at T_{OM} between the

EL (disordered) and the crystal (ordered); see the vertical dashed line at T_{0M} in Figure 2. In equilibrium, it is customary to introduce an unrestricted *partition function* Z , which exhibits a singularity at T_{0M} [14]. If the transition is somehow avoided such as during supercooling in which we continue from the equilibrium to the ESCL, then one describes such a process by considering the restricted ensemble involving $\mathcal{D}$ [15]. The corresponding restricted partition function $Z_{\mathcal{D}}$, as noted above, does not exhibit any singularity at T_{0M} as both sides represent the same (disordered) state corresponding to $\rho = 0$. By considering the restricted partition function $Z_{\overline{\mathcal{D}}}$ involving ordered microstates ($\rho \neq 0$), which again does not show any singularity, and comparing the two free energies $F_{\mathcal{D}} = -T \ln Z_{\mathcal{D}}$ and $F_{\overline{\mathcal{D}}} = -T \ln Z_{\overline{\mathcal{D}}}$, we identify T_{0M} by their crossing. The singularity at T_{0K} , the sharp kink in Figure 3b, is due to a *phase transition* between the ESCL and the ideal glass in the restricted ensemble involving $\mathcal{D}$.

If we introduce $\mathcal{D}'$ as the set of disordered microstates from which we remove all microstates belonging to $\overline{\mathcal{D}}$ associated with the ideal glass, then the corresponding partition function $Z_{\mathcal{D}'}$ can be used to describe the ESCL without any singularity at T_{0K} ; above T_{0K} , $\mathcal{D}'$ is inconsequential [15] so $F_{\mathcal{D}} = F_{\mathcal{D}'}$. In particular, we see from Figure 2 that the ESCL volume V_{ESCL} obtained by using $\mathcal{D}'$ will show no singularity at T_{0K} and can be continued *mathematically* to lower temperatures, except that V_f will become negative under this continuation. Thus, the continuation does not give a physical state, which is reminiscent of the Kauzmann paradox. The singularity at T_{0K} is inferred by the crossing of the free energies $F_{\mathcal{D}'} = F_{\mathcal{D}}$ and $F_{\overline{\mathcal{D}'}}$. It is the absence of a singular behavior in $F_{\mathcal{D}'}$ that is of primary interest here. This is also reflected in the absence of a singularity in the corresponding entropy $S_{\mathcal{D}} = S_{\mathcal{D}'} = -\partial F_{\mathcal{D}'} / \partial T$.

3.2 Absence of a Singularity in Laboratory Glasses

The relaxation time τ of the system, which is independent of τ_{exp} , usually increases monotonically with ζ_0 ; see the upper axis in Figure 2. The SCL remains in equilibrium in $\mathcal{D}$ shown by the solid curve as long as $\tau < \tau_{\text{exp}}$, but begins to fall out of the restricted equilibrium at T_{0g} and becomes a NESCL as soon as $\tau_{\text{exp}} < \tau$. The system is not really frozen yet, but eventually turns into a glass when $\tau > \tau_{\text{exp}}$ at a somewhat lower temperature T_{0G} (not shown in Figure 2, but shown in Figure 3a, where we show the entropy), when the system has no discernible mobility. The loss of mobility results in “freezing” of the system *without* any singular changes in its thermodynamic densities in the GT region $\Delta T_G \doteq (T_{0g} - T_{0G})$. The state below T_{0G} is identified as a glass. There are

no singularities at the GT temperatures of the two laboratory glasses in Figure 2 or the laboratory glass in Figure 3a. The respective curves smoothly connect with the ESCL. Thus, the *experimental glass transition* should be thought of as a crossover phenomenon with a gradual turnover of the ESCL through a NESCL into a glass over a temperature range. As the curves emerge out of the ESCL continuously, there is no mathematical singularity for the top two curves in Figure 2.

3.3 Ideal Glass: Analytic Continuation

The continuous curve in Figure 3a shows $S_{\mathcal{D}} = S_{\mathcal{D}'} = S_{\text{ESCL}}$ of the ESCL. The dotted curve shows S_{GS} , which extrapolates to a positive value of the residual entropy S_R at absolute zero [15]. In contrast, it is commonly believed that S_{SCL} extrapolates to zero at $T_0 = 0$, even though there are no thermodynamic requirements for this.

While Figure 3a does not show any IGT, Figure 3b does at $T_{0K} > 0$, where S^{comm} vanishes. At this point, the ESCL will undergo a phase transition into the ideal glass. We see that the ideal glass has a zero communal heat capacity (heat capacity associated with S^{comm}), but the ESCL has a nonzero communal heat capacity. Thus, the ideal glass and the ESCL are distinct states. As noted above, the transition will result in a singularity in the thermodynamic free energy. Despite this singularity, each state itself is nonsingular in the restricted ensemble. For example, S_{ESCL} can be mathematically extended to temperatures below T_{0K} , although it will result in negative S^{comm} . This is similar to the Gibbs–DiMarzio theory, in which analytically continued $S_{\text{ESCL}}^{\text{conf}}$ becomes negative below the IGT.

4 Nonequilibrium Formulation: Brief Review

The nonequilibrium formulation presented here is a condensed version of our previous presentation elsewhere [11, 16]. The system that undergoes vitrification is represented by Σ . We treat it as an interacting system by embedding it in a medium $\tilde{\Sigma}$; their combination forms an isolated system Σ_0 . Quantities pertaining to Σ_0 will have a suffix 0, while those for $\tilde{\Sigma}$ will have a tilde; quantities for Σ will have no suffix. The medium is taken to be extremely large compared to Σ so that the latter does not affect the fields of $\tilde{\Sigma}$. Thus, its fields $\tilde{T}$, $\tilde{P}$, etc., will be denoted by T_0 , P_0 , etc., of Σ_0 . We will also find it convenient to use the term body to denote any one of Σ , $\tilde{\Sigma}$, and Σ_0 . The quantities pertaining to a body will not have any suffix.

Let Σ be in a nonequilibrium state such as a glass. Its entropy $S(t)$ must obey the second Law, i.e. the Law of increase of entropy, according to which the *irreversible* (denoted by a suffix i) entropy $d_i S$ generated in any infinitesimal physical process within a body satisfies the inequality $d_i S \geq 0$; the equality occurs for a reversible process. This entropy is generated within the system because of dissipative processes. Thus the suffix i can also stand for “internal.” The quantity $d_e S$ with a suffix “e” will denote the entropy exchange with the medium (the “exterior”). In general, we can identify $d_e X$ and $d_i X$ for the change $dX = d_e X + d_i X$ in any extensive quantity X . Therefore, $dS = d_e S + d_i S$. As there is no *exchange* entropy change ($d_e S_0 = 0$) for Σ_0 , we have $dS_0 = d_i S_0 \geq 0$ during any process. For Σ_0 in equilibrium, $dS_0 = 0$ so that $S_0 = \text{constant}$.

4.1 Concept of a Nonequilibrium State and of Internal Equilibrium

4.1.1 An Isolated Body

For Σ_0 in equilibrium, S_0 can be expressed as a *state function* $S_0(\mathbf{X}_0)$ of its extensive observables (E_0 , V_0 , N_0 , etc., that can be controlled by an observer) denoted by $\mathbf{X}_0$, from which follows the Gibbs fundamental relation for the entropy S_0 ,

$$dS_0 = \sum_p (\partial S_0 / \partial X_{0p}) dX_{0p}; \quad (7)$$

the partial derivatives are related to the constant *fields* of the system:

$$(\partial S_0 / \partial E_0) = 1/T_0, (\partial S_0 / \partial V_0) = P_0/T_0, \dots \quad (8)$$

As $\mathbf{X}_0$ remains constant, S_0 remains constant and has the maximum possible value given by the Boltzmann formula $S_0(\mathbf{X}_0) \equiv \ln W_0(\mathbf{X}_0)$, where $W_0(\mathbf{X}_0)$ is the number of microstates corresponding to the observable $\mathbf{X}_0$. This conclusion about the entropy when it is a state function will play an important role below.

For Σ_0 out of equilibrium, S_0 is no longer a constant. The nonequilibrium state will continuously change, which is reflected in its entropy increase in time. This requires expressing its entropy as $S_0(\mathbf{X}_0, t)$ with an *explicit time-dependence*. If it happens that the changes in S_0 and the state come from the variations of additional independent variables, whose set is denoted by ξ_0 , that keep changing with time until the body comes to equilibrium [21, 22], then S_0 can be expressed as a function of $\mathbf{X}_0$ and ξ_0 with no explicit time dependence: $S_0(\mathbf{Z}_0(t))$, where $\mathbf{X}_0$ and ξ_0 is collectively written as $\mathbf{Z}_0$. As the variables in ξ_0 continue to change in time for the isolated system, they cannot be controlled by the observer; thus, they are known as the *internal variables*. We can identify $\mathbf{Z}_0(t)$ as the set of *nonequilibrium state variables* so that the

entropy becomes a state function of $\mathbf{Z}_0(t)$. We can extend Eq. (7) to

$$dS_0 = \sum_p (\partial S_0 / \partial Z_{0p}) dZ_{0p}; \quad (9)$$

the new derivatives $(\partial S_0 / \partial \xi_{0p})$ determine the *affinities* $A_{0p}(t)$,

$$(\partial S_0 / \partial \xi_{0p}) = A_{0p}(t) / T_0(t). \quad (10)$$

All fields and affinities continue to change in time until Σ_0 reaches equilibrium. As Σ_0 comes to equilibrium, all $A_{0p}(t)$ vanish, which requires that ξ_0 are no longer independent of $\mathbf{X}_0$.

A body for which the entropy has become a state function of $\mathbf{Z}_0(t)$ is said to be in *internal equilibrium*. As there is no explicit time dependence, the entropy in internal equilibrium remains constant for the given state variables. The situation is no different than when Σ_0 was in equilibrium. Thus, $S_0(\mathbf{Z}_0(t))$ in this case has its maximum possible value for given $\mathbf{Z}_0(t)$, and is given by the Boltzmann form $S_0(\mathbf{Z}_0(t)) \equiv \ln W_0(\mathbf{Z}_0(t))$, where $W_0(\mathbf{Z}_0(t))$ is the number of microstates corresponding to the state variable $\mathbf{Z}_0(t)$. For a body not in internal equilibrium, the entropy must retain an explicit time-dependence so that the derivatives in Eq. (8) *cannot* be identified as state variables like, temperature, pressure, etc.

4.1.2 An Interacting Body

An interacting body (a body in a medium) out of equilibrium with its medium will also require internal variables. For the body in internal equilibrium, the derivatives $((\partial S / \partial E) = 1/T(t), (\partial S / \partial V) = P(t)/T(t), (\partial S / \partial \xi_p) = A_p(t)/T(t) \dots)$ of its entropy S give the fields $T(t)$, $P(t)$, $A_p(t) \dots$ etc. The corresponding Gibbs fundamental relation is given by

$$dS(t) = \sum_p (\partial S / \partial Z_p) dZ_p. \quad (11)$$

4.1.3 A Simple Example for an Internal Variable

Consider an isolated body Σ_0 formed by two parts Σ_1 , Σ_2 that are initially at different temperatures $T_1(0)$ and $T_2(0)$. We imagine their volumes and particle numbers as fixed, but allow their energies $E_1(t)$, $E_2(t)$ to change with time through their mutual thermal contact. We know that eventually, they come to equilibrium at the same common temperature T_{0f} . During this time, their temperatures keep changing. The total energy $E_0 = E_1 + E_2$ is constant. The entropy S_0 is the sum of the entropies S_1 and S_2 of the two parts. Thus, S_0 is a function of two variables $E_1(t)$, $E_2(t)$. If we want to express S_0 as a function of E_0 , we need another *independent* variable $\xi_0(t)$, which is evidently a function of the difference $E_1(t) - E_2(t)$. We take $\xi_0(t) \equiv [E_1(t) - E_2(t)]/2$. This makes S_0 a function of E_0 and ξ_0 . The affinity $A(t) = \partial S_0 / \partial \xi_0$ is

$$A(t) = 1/T_1(t) - 1/T_2(t)$$

and vanishes in equilibrium, as expected. Here, $T_1(t)$ and $T_2(t)$ are the instantaneous temperatures of the two parts and are given by $1/T_1(t) = (\partial S_1/\partial E_1)$, $1/T_2(t) = (\partial S_2/\partial E_2)$.

4.2 Gibbs Free Energy of an Interacting System

From now on, we will only consider the system in internal equilibrium. We will further simplify our discussion by mostly considering one internal variable ξ and restrict the observables to E , V , and N for simplicity. Moreover, we will keep N fixed so that it will not be shown explicitly and allow the possibility of fluctuating E and V due to exchanges with the medium. The medium is always taken to be in equilibrium with its fields and affinity given by T_0, P_0 and $A_0 = 0$; the system achieves these values when it comes to equilibrium with $\tilde{\Sigma}$. In terms of $H(t) \equiv E(t) + P_0 V(t)$, $G(t) \equiv H(t) - T_0 S(t) = E(t) - T_0 S(t) + P_0 V(t)$, which are the time-dependent enthalpy and the Gibbs free energy, respectively, of the system Σ , it is easy to show that [22]

$$S_0(t) - \tilde{S}_0 = S(t) - H(t)/T_0 = -G(t)/T_0, \quad (12)$$

where $\tilde{S}_0 \equiv \tilde{S}(E_0, V_0, \xi_0)$ is a constant, which is independent of the system. Here, $S(t)$ and $S_0(t)$ are the entropies of Σ and Σ_0 . It immediately follows from this that $dG/dt = -T_0 d_i S_0/dt \leq 0$, as expected. We similarly have $dH/dt = T_0 d_e S/dt = d_e Q/dt$, where $d_e Q = T_0 d_e S$ is the heat exchange with $\tilde{\Sigma}$.

4.3 Thermodynamic Forces for Relaxation

The Gibbs fundamental relation can be written as

$$dE(t) = T_0 dS(t) - P_0 dV(t) + (T(t) - T_0) dS(t) - (P(t) - P_0) dV(t) - A(t) d\xi(t). \quad (13)$$

Using the first Law $dE(t) = T_0 d_e S(t) - P_0 dV(t)$, we find

$$T_0 d_i S(t) = (T_0 - T(t)) dS(t) + (P(t) - P_0) dV(t) + A(t) d\xi(t) \geq 0. \quad (14)$$

Each of the three terms on the right must be non-negative in accordance with the second Law

$$(T_0 - T(t)) dS(t) \geq 0, (P(t) - P_0) dV(t) \geq 0, A(t) d\xi(t) \geq 0. \quad (15)$$

The prefactor $T_0 - T(t)$, etc., in each equation represents a *thermodynamic force* that drives the system toward equilibrium.

5 Nonequilibrium Relaxation in Internal Equilibrium

5.1 Thermodynamic Relaxation

During isobaric vitrification, the system Σ , originally in equilibrium with a medium at T'_0, P_0 , is suddenly brought into another medium at T_0, P_0 at time $t = 0$. As Σ is out of equilibrium, it will strive to equilibrate irreversibly ($d_i S/dt > 0$). The resulting process is called relaxation during which various thermodynamic quantities will undergo irreversible changes dictated by the second Law, which we now investigate.

5.1.1 Heuristic Consideration

As Σ has no time to interact with the new medium at $t = 0$, its initial temperature $T(0)$ is the original temperature T'_0 . As Σ eventually comes to equilibrium, we must have $T(\tau_{eq}(T_0)) = T_0$, where $\tau_{eq}(T_0)$ is the time required to come to equilibrium. Thus, $T(t)$ continues to fall during relaxation from T'_0 to T_0 . Accordingly, the heat exchange $d_e Q = dH < 0$. Thus, the enthalpy decreases during relaxation, which is an experimental fact [2]. Similarly, the initial entropy $S(0)$ is the entropy $S_{ESCL}(T'_0)$ of the higher temperature. After equilibration, $S(\tau_{eq}(T_0)) = S_{ESCL}(T_0)$. Since the entropy increases with temperature, we conclude that the entropy also falls during relaxation from $S_{ESCL}(T'_0)$ to $S_{ESCL}(T_0)$ at $t = \tau_{eq}(T_0)$.

5.1.2 Thermodynamic Support

We now support this intuitive picture by the nonequilibrium thermodynamics of the previous section. Here, we closely follow [22]. It is easy to see from Eqs. (13) and (14) that

$$\begin{aligned} \frac{d_i S(t)}{dt} &= \left(\frac{1}{T(t)} - \frac{1}{T_0} \right) \frac{dE(t)}{dt} + \left(\frac{P(t)}{T(t)} - \frac{P_0}{T_0} \right) \frac{dV(t)}{dt} + \left(\frac{A(t)}{T(t)} \right) \frac{d\xi(t)}{dt}. \end{aligned} \quad (16)$$

Each term on the right side must be nonnegative in accordance with the second Law. Let us assume that in an *isobaric* vitrification, $P(t) = P_0$. In this case, we find by combining the first two terms in Eq. (16) that

$$(1/T(t) - 1/T_0) dH(t)/dt \geq 0. \quad (17)$$

As $dH(t)/dt < 0$ experimentally [2] and theoretically as noted above,

$$T(t) > T_0 \quad (18)$$

during relaxation so that $T(t)$ approaches T_0 from above [$T(t) \rightarrow T_0^+$]. It now follows from the first inequality in Eq. (15) that during vitrification

$$dS(t)/dt \leq 0. \quad (19)$$

A more refined and general argument for the validity of Eq. (19) is also available [11].

5.2 Microstate Probabilities in Internal Equilibrium

For a body in internal equilibrium, the situation is very similar to that of a body in equilibrium. Thus, the maximization of entropy results in a very similar formulation of the microstate probabilities. The equilibrium probabilities are given by $p_{keq} = \exp[-\beta_0(E_k + P_0 V_k)]/Z_{eq}$, where Z_{eq} is the equilibrium partition function, $\beta_0 = 1/T_0$, and E_k , V_k are the energy and volume of the k th microstate. For the body in internal equilibrium, the microstate probabilities are given by

$$p_{ki-eq} = \exp[-\beta(t)\{E_k + P(t)V_k + \mathbf{A}(t) \cdot \boldsymbol{\xi}_k\}]/Z_{i-eq}, \quad (20)$$

where Z_{i-eq} is the internal equilibrium partition function; $\beta(t) = 1/T(t)$, and $\boldsymbol{\xi}_k$ is the set of internal variables for the k th microstate. The particle number N , which is held fixed in both cases, is not shown. In terms of the number of microstates $W(E, V, \boldsymbol{\xi})$ corresponding to E , V and $\boldsymbol{\xi}$, Z_{i-eq} is given by

$$Z_{i-eq} = \sum_{E, V, \boldsymbol{\xi}} W(E, V, \boldsymbol{\xi}) \exp[-\beta(t)\{E + P(t)V + \mathbf{A}(t) \cdot \boldsymbol{\xi}\}]; \quad (21)$$

it differs from Z_{eq} due to the presence of $\boldsymbol{\xi}$ and time-dependent fields/affinities.

6 The Free Volume and the Communal Entropy

6.1 The Cell Theory

The simplest model to account for the nonzero particle size is described by the van der Waals' equation

$$(P + N^2 a/V^2)(V - Nb) = NT,$$

where a accounts for the intermolecular attractive forces and the "free volume" is given by $V - Nb$. The parameter b is half the volume of a sphere of radius $2r_0$, where r_0 is the "radius" of the particle [14]. It is the excluded volume for each particle and the presence of N in Nb implies its additivity. Indeed, it should be thought of as the "thermodynamic" volume of a particle, which is determined by

the interactions with its neighbor. One uses the cell theory of liquids to go beyond the van der Waals theory. Here, V is divided into N cells (such as the Voronoi-type cells) of an average volume Δ per particle (Figure 4), where we show the possible cell arrangement for disordered (liquid or gas) in (a) and ordered (crystal) states in (b). Each cell has a single particle within it as shown. For molecules with connectivity such as polymers (Chapter 8.7), one must take proper care of all *distinct* placements of monomers that respect their connectivity. For example, if we consider a disordered conformation of a polymer with 17 monomers, then we must consider all distinct conformations of the polymer even though each conformation has a single monomer in the 17 cells in (a). Thus, there will be many more microstates for the cell pattern in (a) when connectivity has to be incorporated. There will be a single microstate if there is no connectivity to consider. This poses no conceptual problem as the average of any observable O in the cell model is given by the standard formulation $\bar{O} \equiv \sum_k O_k p_{ki-eq}$, where O_k is the value of O for the k th microstate and the sum is over all *distinct* microstates. It is then clear that the entropy associated with local motion in the cell potential also contains what is commonly known as the *conformational entropy* due to different conformations of a molecule such as a polymer.

The nonuniform model in (a) for the disordered state is a generalization of the uniform model traditionally used in cell theories. The other difference is that we allow for an internal variable. The motion of each particle within its cell is governed by ϕ due to all its neighbor, which we denote by $\phi(\mathbf{r}|\{\mathbf{r}'(t)\})$, where $\mathbf{r}$ is the position of the particle under consideration within its cell and $\{\mathbf{r}'\}$ denotes the set of the continually changing positions of all its neighbors in time. The connectivity among the

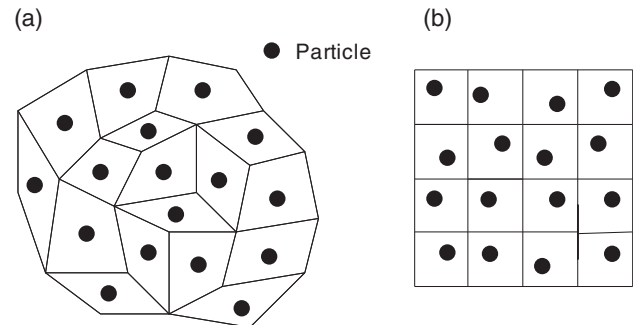


Figure 4 Cell representation of a small region of disordered (a) and ordered (b) configurations at full occupation: each cell contains a particle. Each cell representation uniquely defines a potential well or basin in the potential energy landscape. Each particle is surrounded by four particles in the ordered configuration, but not for the disordered configuration. In the hole theory, some of the cells remain empty.

neighbors and the particle must be properly accounted for in this set. The probability $P(\phi)$ for the potential $\phi(\mathbf{r}|\{\mathbf{r}'(t)\})$ is given by the following identity

$$P(\phi) = \sum_k' p_{ki-\text{eq}} \quad (22)$$

where the prime over the sum implies that the sum is restricted to those microstates in which the particle and its neighbors are restricted to be at $\mathbf{r}$ and $\mathbf{r}'$, respectively.

The volume Δ must be at least as big as needed to allow for the local oscillations. The cell potential can be used to characterize the *interaction volume* v_i : it is the minimum volume needed for the allowed local motion. One way to quantify v_i is by the root-mean square of the displacement during the local motion as follows. The average over all possible cell potentials with probability $P(\phi)$ of the displacement squared is given by

$$r_{\text{rms}}^2 \equiv \sum_{\phi} P(\phi) \left[\frac{1}{\tau_{\phi}} \mathbf{r}^2(t) dt \right], \quad (23a)$$

where $\mathbf{r} = 0$ is taken to be at the minimum of the potential. The inner integral is over the time period τ_{ϕ} of an oscillation controlled by ϕ . We first observe that r_{rms} changes with the temperature. To see this most clearly, we simply consider an interparticle harmonic potential ϕ . From dimensional analysis alone, we conclude that the mean square displacement of all the particles scales as the temperature: $\overline{r^2} \sim T(t)/k_s$, where k_s is the spring constant of the potential. Thus,

$$r_{\text{rms}}(T(t)) \sim [T(t)/k_s]^{1/2}, \quad (23b)$$

and vanishes at absolute temperature $T(t) = 0$. It usually happens that the oscillatory modes equilibrate rapidly with the medium. In that case, we must replace $T(t)$ by T_0 . At absolute zero, particles are sitting in the potential minima, and there is an average distance d_{min} between particles. Half of the average distance $r_{\text{min}} \equiv d_{\text{min}}/2$ is taken as the “radius” of the particle, which then determines its interaction volume v_m at absolute zero. This is the minimum of the interaction volume. The distance r_{min} should not be confused with the so-called radius r_0 of a particle corresponding to the “impenetrability” of the particles. The interparticle potential begins to rise steeply for separation between particles below the “radius” r_0 [14]. Thus, r_0 is not strictly the radius of a particle. As the temperature increases, the linear size of the particle increases due to oscillations and so does its interaction volume, which is now given by

$$v_i = \gamma(r_{\text{min}} + r_{\text{rms}})^3 \quad (24)$$

in terms of a geometrical factor γ of order unity. The above volume may be quite different from the customarily defined occupied volume v_o , which is commonly used

in the glassy literature. Unfortunately, there is a lot of ambiguity in the definition of v_o and how to obtain it theoretically [19] so we make no attempt to compare the two.

The difference $v_f = \Delta - v_i$ is the free volume v_f that is the elbow room for the translation and rotation of the center of mass of the particle. This motion gives rise to the diffusion of the particle from the region over which the local oscillatory motion occurs. As ζ_0 decreases, the elbow room, i.e. v_f increases (and so do Δ and v_i) but not so much so that particles are still confined within their respective cells. As the free volume increases further, the particles can escape to the neighboring cells so that sometimes a cell may have multiple occupancy of the particles. The particles will undergo local motion in the new cell before they make excursion to another neighboring cell. If the free volume increases too much, then diffusion becomes the dominant motion and the local motion is no longer possible as the particles are far apart now. A situation like this occurs in gases. The above is an average picture so that it will also occur through to fluctuations in energy, volume, and internal variables. The aforementioned scenario has been confirmed by numerical simulations that has been discussed by several authors; see, for example, Refs. [1, 22] and Figure 1.

The above discussion is equally valid for the disordered and ordered macrostate. We will, however, consider the disordered macrostate in the following.

An obvious refinement of the above cell theory is to allow for holes by having some empty cells. Their presence gives an additional contribution to the free volume. It also allows for a considerable variation in the number of neighboring particles due to the presence of holes, which makes this theory attractive. As the volume of a glass is considerably greater than that of the corresponding crystal or the ESCL, the glass has a significant number of holes, which decreases during relaxation. In general, the decrease in the free volume is related to the irreversible relaxation, whereas the decrease in the interaction volume is related to the equilibrium relaxation as noted above since the local motion within the cell potential occurs at the temperature T_0 of the medium and not at the instantaneous temperature of the glass; see also the discussion by Matsuoka [19]. The division of volume in the interaction and free volumes results in the two volumes to be independent as they refer to independent degrees of freedom. Their existence may be related to the success of the two-parameter model of Aklonis and Kovacs [23].

6.2 Communal Entropy

The communal entropy S^{comm} plays a central role in the study of glasses [1, 15, 17]. From the fact that entropy and

volume are both extensive, we find that the entropy density $\sigma = S/V$ is a *homogeneous function* of order zero. We can write the entropy as a sum of two terms: $S = V_i\sigma + V_f\sigma$ in which the two volumes must be extensive. This is a trivial identity but allows us to introduce two different entropy components associated with the two components of the volume. One such component is S^{comm} , which is associated with the translation of the particles. The free volume decreases as ζ_0 increases and inhibits the translation. The particles must be fully jammed if there is no elbow room ($V_f = 0$). In this state, there cannot be any translation and S^{comm} must also vanish. This identifies the ideal glass. If we wish to identify the communal entropy associated with the free volume, then it must vanish for the ideal glass. The only possible relationship between S^{comm} and V_f must be *linear* because of their extensivity. If we write it as $S^{\text{comm}} = V_f\sigma'$ with $\sigma' \neq \sigma$, then the other component $S^{\text{int}} = S - S^{\text{comm}}$, the interaction entropy, is given by $S^{\text{int}} = V_i\sigma + V_f(\sigma - \sigma')$. As S^{int} must be determined by the local motion within the cell potential ϕ , it depends on V_i but not on V_f . Hence, we take $\sigma' = \sigma$ and write

$$S(t) = S^{\text{int}}(t) + S^{\text{comm}}(t), S^{\text{comm}} = V_f\sigma, S^{\text{int}} = V_i\sigma; \quad (25)$$

each of the above two components of the entropy must be non-negative and must satisfy the second Law provided there is minimal coupling between the two kinds of motion. As said earlier, S^{int} includes the conformational entropy associated with different conformations of the molecules. The deep connection that we have discovered between the free volume and communal entropy shows that they vanish simultaneously in the ideal glass so that whether we vary the density (control variable P_0) or the entropy (control variable T_0), we obtain the unique ideal glass at the respective Kauzmann point. This, we hope, will clarify some confusion present in the field as we discuss now.

7 The Unifying Approach for Glasses

It becomes clear from the above discussion that one can consider several entropy differences (S_{ex} , S^{conf} , S^{comm} , etc.). Some will vanish, most probably at different ζ_0 , under extrapolation to higher ζ_0 . Similarly, various definitions of the free volume will also show that they vanish at different ζ_0 under extrapolation. Thus, unless care is taken, the vanishing of the entropy difference and the free volume will appear to be unrelated. This has created much confusion in the field. However, by a careful definition of the free volume and the relevant (communal) entropy, one ensures that they vanish simultaneously at

a point called the IGT point. At this point, they refer to the same unique macrostate; see Figures 2 and 3.

In the following, we are interested in the SCL in $\mathcal{D}'$. We will focus on the communal entropy for which we use S instead of S^{comm} for notational simplicity. We will exhibit E and suppress all other extensive observables below and use a single internal variable ξ for simplicity. According to the second Law $S_{\text{NESCL}}(E, \xi) < S_{\text{ESCL}}(E)$; see Figure 5 where various portions of entropy curves are also identified. As the slope of the curve FG determines the inverse of the internal temperature $T(t) \neq T_0$ of a NESCL, while that of the curve DFCK the inverse of the medium temperature T_0 , we conclude from the figure that $T_G(t)$ at E_G is higher than $T_K = T_{0K}$ at E_K . Indeed, as $T_{\text{NESCL}}(E) = T_{\text{ESCL}}(E)$ at $E = E_F$ and at $E = E_K$, where E_F is the energy at F, it is evident that $T_{\text{NESCL}}(t) > T_{0K}$ over FG. Here, we have used $E(t)$ to express $T(E)$ as $T(t)$. As $S_{\text{NESCL}}(E, V, \xi)$ has no singularity over its entire range KGF, we can expand $S_{\text{NESCL}}(E, V, \xi)$ in the form of a Taylor series over FG around the point K. For later applicability, it is useful to consider $S_{\text{NESCL}}(E, V, \xi)$ as a function of $T(t)$, $P(t)$ and $\xi(t)$. For the isobaric vitrification at P_0 that we are considering, we set $P(t) = P_0$. Introducing $\Delta T(t) \equiv T(t) - T_{0K}$ and $\Delta\xi(t) \equiv \xi(t) - \xi_{\text{eq},K}$ and recognizing that at K the heat capacity C_{PK} is nonzero but finite and that the affinity A_{0K} vanishes (as the ESCL represents equilibrium states in $\mathcal{D}'$), we immediately conclude that the leading terms in the expansion must be linear in $\Delta T(t)$ (no linear term in $\Delta\xi(t)$) and bilinear in $\Delta T(t)\Delta\xi(t)$. Thus, we can pull out ΔT from all the expansion terms to finally write in terms of a function Ψ_S whose definition is evident from the (infinite) Taylor expansion ($S_{\text{ESCL}}(E_K) = 0$):

$$S_{\text{NESCL}}(T(t), P_0, \xi(t)) = \Delta T(t)\Psi_S(T_{0K}, P_0, \Delta T(t), \Delta\xi(t)); \quad (26)$$

we have not shown any dependence on $\xi_{\text{eq},K}$ as it is a function of T_{0K} , P_0 so it is no longer independent. The extensive function takes the value $\Psi_S(T_{0K}, P_0, 0, 0) = C_{PK}/T_{0K}$.

A similar Taylor expansion can be made for the volume V_{NESCL} . We first recall that $V_{f,\text{NESCL}}$ and the communal entropy S_{NESCL} vanish simultaneously and that

$$S_{\text{NESCL}}(T(t), P_0, \xi(t)) = \sigma(T(t), P_0, \xi(t))V_{f,\text{NESCL}}(T(t), P_0, \xi(t)). \quad (27)$$

(In contrast, there is no such relationship between the configurational entropy and the free volume. The simplest way to appreciate is to recognize that the configurational entropy in the Gibbs–DiMarzio theory [18] is nonzero even when the polymers cover the entire lattice, which corresponds to zero free volume.) Thus, $V_{f,\text{NESCL}}$ is also non-singular and will have a Taylor expansion

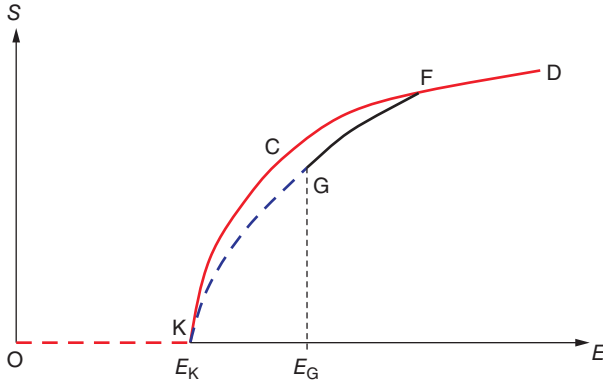


Figure 5 Schematic form of communal entropies in $\mathcal{D}'$ for the equilibrium supercooled liquid and the nonequilibrium supercooled liquid in accordance with the second Law and the gap hypothesis [15]. The lowest possible energy of the equilibrium supercooled liquid is E_K and the corresponding entropy is given by the curve KCDF. It vanishes at K without any singularity. The point K represents the unique ideal glass whose entropy remains zero as shown by the ideal glass entropy OK (dashed line). The lowest possible energy of the nonequilibrium supercooled liquid, which emerges continuously out of the equilibrium supercooled liquid at point F, is shown to be $E_G > E_K$ at point G due to additional defects. It represents the entropy of a laboratory glass; it also has no singularity at point G so that it can be mathematically continued below E_G until it vanishes. As the disordered state of zero entropy must be unique, this continuation must terminate at point K with the same slope as of the curve KCDF. It is shown by the dashed curve GK. It is in essence similar to the continuation carried out by Kauzmann but for S^{comm} . We do not show the axis corresponding to the independent variable ξ , which is changing along the curve FG. (At points K and F, ξ is no longer independent). The slope at point G is lower than that at point K.

around the Kauzmann point. To determine the nature of the expansion, we follow the above method to determine the leading powers of $\Delta T(t)$ and $\Delta \xi(t)$. The volume expansion coefficient at K due to the free volume is nonzero as we approach K from the high temperature side because of the difference in the slopes at K in Figure 2. Thus, the expansion must start with a term linear in $\Delta T(t)$. The determination of the leading power of $\Delta \xi(t)$ requires considering the behavior of $(\partial V / \partial \xi)_{T,P}$. By considering the double Legendre transform $\hat{G} = E - T(t)S(t) + PV(t)$, which is a system-intrinsic internal Gibbs free energy, we find that $V = (\partial \hat{G} / \partial P)_{\xi,T}$ so that

$$(\partial V / \partial \xi)_{T,P} = (\partial^2 \hat{G} / \partial \xi \partial P) = (\partial A / \partial P)_{\xi,P};$$

we emphasize that $\hat{G}$ (even with $P = P_0$ as noted above) should not be confused with the Gibbs free energy $G(t) = E(t) - T_0 S(t) + P_0 V(t)$, which contains the temperature and pressure of the medium [14, 22]. It is the latter that decreases in a spontaneous process as discussed in Section 4.2. As the affinity A always vanishes at

K regardless of the pressure, the derivative on the right side vanishes at K. This means that $(\partial V / \partial \xi)_{T,P}$ also vanishes at K, which leads to a leading bilinear combination $\Delta T(t) \Delta \xi(t)$. Thus, the situation is as before for S_{NESCL} so that we can write a similar form for $V_{f,\text{NESCL}}$,

$$V_{f,\text{NESCL}}(T(t), P_0, \xi(t)) = \Delta T(t) \Psi_V(T_{0K}, P_0, \Delta T(t), \Delta \xi(t)). \quad (28)$$

We can use this form of the free volume in the Doolittle Eq. (5) to obtain

$$\eta = \eta_0 \exp(\gamma v_m / (T(t) - T_{0K}) \psi_V) \quad (29)$$

in terms of the intensive function $\psi_V \equiv \Psi_V / N$. We thus conclude that the phenomenological equation is a special case of the above general equation. The limited validity of the original (constant parameters) Doolittle equation also makes the VTF equation with limited validity. In addition, different concept of the free volume will also yield different temperatures where it vanishes. This explains the puzzling differences between T_{0V} and the Kauzmann temperature noted by several workers.

Using the linear relationship from Eq. (27) in Eq. (5), we obtain

$$\eta = \eta_0 \exp(\gamma v_m / g S_{\text{NESCL}}) \quad (30)$$

in terms of the per particle communal entropy $s_{\text{NESCL}} \equiv S_{\text{NESCL}} / N$ and $g = 1/\sigma$. This is the analog of the Adam–Gibbs Eq. (3) in terms of the communal entropy, except that the viscosity diverges at different temperatures in the two formalism. A similar argument as used above will also show that in terms of $\Delta T_S(t) \equiv T(t) - T_{0S}$,

$$S_{\text{NESCL}}^{\text{conf}}(T(t), P_0, \xi(t)) = \Delta T_S(t) \Psi_S^{\text{conf}}(T_{0S}, P_0, \Delta T_S(t), \Delta \xi(t)).$$

Thus, its vanishing at T_{0S} also shows a divergence of viscosity in Eq. (3).

As all these formalisms are developed based on different approaches but with the same conclusion of diverging viscosity, it appears that the suggestion of a rapid rise in the viscosity due to a sudden drop in some form of entropy difference seems very enticing. Thus, we are driven to the conclusion that we can treat the SCL GT within a thermodynamics formalism involving some sort of entropy crisis. However, the divergences occur at different temperatures so the divergences may be devoid of any physics in terms of ideal glass. This leaves the nature of the state with a diverging viscosity quite mysterious.

While the vanishing of free volume is not tied to the vanishing of s^{conf} or s_{ex} , it occurs simultaneously with the vanishing of the communal entropy. Thus, our proposal of using the communal entropy ties the divergence of the viscosity with the vanishing of either the free

volume or the communal entropy at the same temperature T_{0K} , and helps in elucidating the nature of ideal glass as a *jammed* state with no translational mobility and, hence, no communal entropy.

8 Perspectives

A complete understanding of viscosity divergence around GT is of technological importance. The conventional approaches to study viscosity as a function of temperature either uses ΔS_{ex} , S^{conf} , or V_f . Phenomenological data fitting invariably leads to a perplexing scenario in that the divergence occurs at different temperatures and does not unravel the root cause of the dynamical slowdown. This seems unsettling as the invariable conclusion is that there is no relationship between the vanishing of V_f , ΔS_{ex} , and S^{conf} as used in the experimental analysis. The puzzle is that the thermodynamic state of the system with a diverging viscosity must be independent of the theory used to describe the system. Such a state must be a unique state in that once the viscosity has diverged, the state cannot change in time unless disturbed.

With our current understanding of nonequilibrium thermodynamics, we have begun to unravel the mystery a bit by connecting the viscosity divergence with either the vanishing of the free volume or the communal entropy. This is done by properly identifying the two concepts thermodynamically. For a system in internal equilibrium, η must be a function of the state variables: $\eta = \eta(T(t), P(t), \xi(t))$. For a state with diverging viscosity, there cannot be any variations in the fields. In other words, we expect a unique temperature where η diverges. At this point, which identifies the Kauzmann temperature T_{0K} , the system mathematically turns into an ideal glass state characterized by vanishing S^{comm} and V_f simultaneously. This mathematical singularity appears as the sudden and rapid rise in the viscosity in laboratory glasses. Thus, the new approach provides a unified picture of the glassy behavior. While we did not discuss it here, we have shown it elsewhere [22] that our nonequilibrium thermodynamics also provides a rationale for the Tool–Narayanaswamy phenomenology (Chapter 3.7). It is evident that we can never get to the ideal state in the laboratory, but this is not relevant for the mathematical expansion around the Kauzmann point.

The linear relation $S^{comm} = V_f \sigma$ associated with the free volume V_f differs from the alternate choice $S_f = -\ln V_f$ used by several authors ([19], for example). We do not consider the latter choice as it cannot only give negative communal entropy, but also does not respect the extensivity of the two quantities.

The limitation of the chapter should be mentioned. We have not discussed recent work dealing with the heterogeneity in space and time for glasses. The reason for this is that the nonequilibrium thermodynamics that we are using requires the additivity of the entropy for different parts. This requires the parts to be macroscopically large so that surface effects can be neglected. Thus, the approach is not applicable to a few particles for which we need small-size nonequilibrium thermodynamics, a field which is in infancy at present. We have also not discussed how the notion of the free volume or the communal entropy can be extended to each microstate as it evolves in time. Such a study will provide more detailed information about the resulting fluctuations going on within the system.

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3.4

Atomic Vibrations in Glasses

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1 Introduction

Atoms have by definition essentially fixed position in a solid. Their only degrees of freedom are thus vibrations around these positions with amplitudes that increase with temperature. As a thermodynamic measure of these changes, the heat capacity then determines the temperature dependence of the internal energy, entropy, and other functions. But the relevance of atomic vibrations is not restricted to thermal properties because thermal energy is involved in any process where potential energy barriers must be overcome. This is the case of not only any kind of phase transformations, including magnetic or ferroelectric transitions, but also of transport of heat, electrically charged species, or atoms.

In a crystal, atoms do not vibrate independently from one another. Vibrations are instead described as a set of harmonic plane waves termed *phonons* whose energies are quantized, whose number and type are determined by the symmetry of the lattice, and whose frequencies vary with the wave vectors according to specific dispersion relations. Although the fundamental basis of *lattice dynamics* was laid down by Born and von Karman as early as 1912, the lack of spatial symmetry prevents this theory from being applied to amorphous solids. The problem of atomic vibrations in glasses has thus long been laid aside until the impressive development of new experimental techniques, computing capabilities, and theoretical advances has made it possible to tackle it fruitfully in the last past decades.

The connection between the macroscopic and microscopic aspects of atomic vibrations is most readily

established through the *vibrational density of states*, $g(\Omega)$, which is the distribution of the number of vibrational modes as a function of the frequency Ω . The vibrational isochoric heat capacity $C_v(T)$ is directly derived from $g(\Omega)$ through

$$C_v(T) = \int_0^{\Omega_m} c_v(\Omega, T) g(\Omega) d\Omega, \quad (1)$$

where Ω_m is the highest vibrational frequency. As for $c_v(\Omega, T)$, it is the heat capacity of a single oscillator given by the Einstein function.

$$c_v(x) = \frac{x^2 e^x}{(e^x - 1)^2}, \quad (2)$$

where $x = \hbar \Omega / k_B T$, and k_B and $\hbar$ are Boltzmann and reduced Planck constants, respectively.

In the last past decades, much progress has been made either theoretically or experimentally to determine $g(\Omega)$ as well as the various vibrational excitations existing in glasses. These advances will thus be reviewed in this chapter with a focus on low-temperature conditions under which a rich phenomenology manifests itself. When heat capacities are approaching their Dulong-and-Petit limits, which is already the case for oxide glasses near room temperature, significant effects of structure and composition on vibrational properties in contrast necessarily tend to vanish. This is why such high-temperature conditions will not be considered in this chapter.

The starting point will be the classical description of phonons in perfectly ordered structures with a simple one-dimensional model. The impact of disorder on the vibrational properties of the system will reveal the loss of the plane-wave character of the normal modes and the concomitant apparition of quasi-localized modes. We follow with the comparison between the low-temperature

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thermal properties of crystalline and disordered solids, underlining the relation between the well-known anomalous behavior of the latter materials and their vibrational properties. Finally, we discuss the implications for vibrational spectroscopy of sound waves and optic modes, including the boson peak.

2 Atomic Vibrations in Disordered Solids

2.1 The Diatomic Linear Chain

A simple system is a chain of N atoms of mass m alternating with N atoms of mass M to which they are connected by springs of force constant K . If periodic conditions are applied, the chain forms an infinite periodic lattice of unit cells comprising one of each mass. The solution to the equation for longitudinal motions is a set of well-defined propagating plane waves with eigenfrequencies Ω_j and associated wave vectors Q_j , which define two dispersion curves $\Omega_j(Q_j)$, namely, an acoustic and an optic branch representing in- and anti-phase motion of the masses within a unit cell, respectively. Each solution j is called a *normal mode* or an *eigenmode*. For the j th normal mode, the displacement of mass l of one species reads

$$U_{j,l}(t) = u_j \exp\left(i\left[Q_j r_l - \Omega_j t\right]\right), \quad (3)$$

where u_j is the amplitude of the mode and r_l is the position of the mass in the chain. At every moment, there exists a perfect spatial oscillatory pattern of the mass displacements $u_{j,l} = u_j \exp(iQ_j r_l)$, characterized by Q_j .

One can then introduce disorder by varying the spring constants K_i along the chain, the masses, or their equilibrium positions. Here, we will assume a normal distribution of spring constants with a mean value K_0 and a standard deviation δK to diagonalize the dynamical matrix and derive the eigenfrequencies and eigenmodes of the system. Owing to disorder, $U_{j,l}$ can no longer be simply expressed as in Eq. (3) so that it is no longer possible to define Q_j strictly. One can nevertheless expand $u_{j,l}$ in a Fourier series of the components Q_k with amplitudes $\alpha_{j,k}$ [1]. For a quasi-plane-wave normal mode j , the amplitude is significant only for $\alpha_{j,k}$ for which $j \approx k$. Conversely, a localized mode has a large range of nonzero $\alpha_{j,k}$. The nature of a normal mode j can thus be roughly characterized by the mean value $\bar{Q}_j$ and the standard deviation of its wave vector spectral density $|\alpha_{j,k}|^2$. These coefficients also control the response of the system to a plane-wave vibrational excitation [1]. As an example, eigenfrequencies Ω_j have been computed for a disordered chain comprising $N = 2000$ masses as a function of $\bar{Q}_j$ (Figure 1) with $\delta K/K_0 = 0.25$ and a mass ratio $M/m = 2$.

As noted long ago [2], the vibrational density of states of the disordered chain $g_d(\Omega)$ is not much affected by disorder, especially for the acoustic modes whose density is actually similar to that of a crystalline counterpart $g_c(\Omega)$. The main differences occur near termed frequencies where $g_c(\Omega)$ exhibits sharp maxima, which are termed *Van Hove singularities* and are smeared out by disorder (Figure 1b). Although this similarity is holding particularly true for optic modes, $g_d(\Omega)$ is higher than $g_c(\Omega)$ by only about 3% even at low frequencies, i.e. in the acoustic regime.

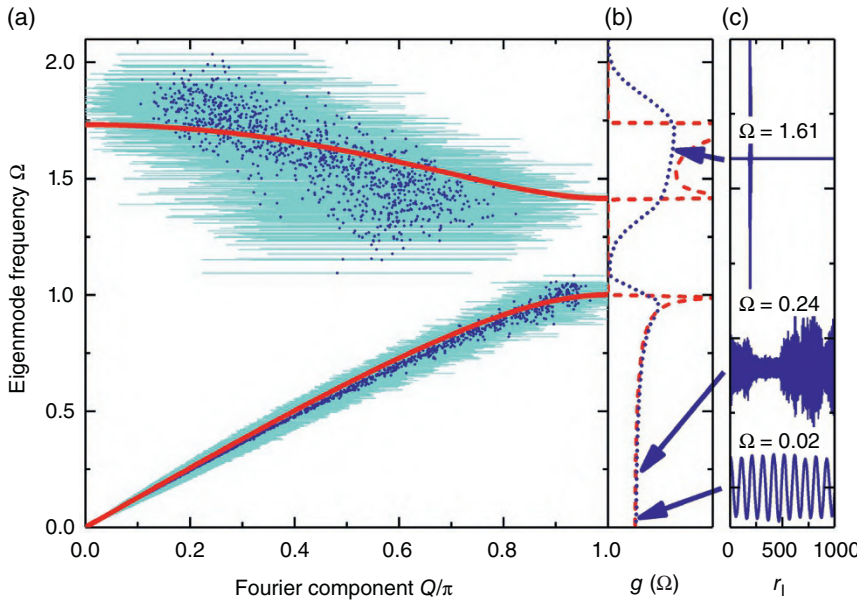


Figure 1 Vibrational properties of a disordered diatomic linear chain. (a) Eigenmode frequencies Ω_j as a function of the mean value $\bar{Q}_j$ of the wave vector spectral density $\alpha_j(Q)$ (dots); standard deviations of $\alpha_j(Q)$ centered on $\bar{Q}_j$ characterizing the Q -spread of the j th eigenmode (very thin horizontal lines); dispersion curves of the acoustic and optic modes of the ordered chain (thick oblique curves). (b) Vibrational density of states $g(\Omega)$ of the crystalline (dashed line, $g_c(\Omega)$) and the disordered chains (dotted line, $g_d(\Omega)$). (c) Displacement snapshots for the three eigenmodes indicated.

In contrast, the nature of the vibrational modes is strongly modified by disorder (Figure 1a and b). The progressive scattering of the initial plane waves is clearly illustrated by the wide Q -spread of the eigenmodes (Figure 1a). As generally found, the higher the frequency, the larger is the deviation from a plane-wave excitation. In the long-wavelength limit, the very low-frequency acoustic modes hardly differ from those of their crystalline counterparts. Details of the force constant distribution is indeed of little concern to these long-wavelength acoustic excitations as fluctuations are averaged out.

The eigenvectors (mass displacements) of these modes exhibit almost perfect oscillations in space as illustrated in Figure 1c by the lowest line corresponding to $\Omega_j = 0.02$. This is no longer true for $\Omega_j = 0.24$ for which the envelope of the mass displacements shows important spatial variations. This mode is still an extended (collective) mode as all the masses participate in the vibration, albeit with different amplitudes. The loss of the plane wave character increases dramatically for modes at higher frequency as shown for $\Omega_j = 1.61$ belonging to the optic branch in the crystalline chain. Most of the vibrational amplitude is localized on a couple of neighboring masses. All high-frequency modes show significant displacements of neighboring masses only, occurring at randomly distributed spatial positions. But these modes are not truly localized because their vibrational amplitudes are extremely small for many masses, but not exactly zero.

2.2 Real Amorphous Solids

Scattering of the vibrational modes thus increases with frequency even when elastic disorder is small enough that the vibrational density of states is similar to that of a periodic lattice. To what extent such a simple picture can be generalized has been much debated because real glasses combine positional, mass, and elastic disorder in complex 3-D structures made up of coupled structural entities. Further, disorder-induced mixing of transverse and longitudinal polarized excitations should arise at high frequency [1].

In the long-wavelength limit, sound waves propagate in glasses as they do in crystals. At that scale, amorphous solids are isotropic continuous elastic media whose low-frequency sound waves can still be reasonably described as quasi-plane-wave acoustic excitations. Phonon-like transverse acoustic excitations showing linear dispersion have been, for example, measured in vitreous silica [ν -SiO₂] up to ~440 GHz [3], which corresponds to a length scale of ~10 nm. This result might thus suggest that the low-temperature thermal properties of glasses should mimic those of their crystalline counterparts, at least below 2–3 K, but this does not seem to be generally the case. From the expected non-plane-wave character of the high-frequency eigenmodes, it is further anticipated

that selection rules should be relaxed in spectroscopic studies, complicating the analysis and limiting the amount of information that can be obtained from vibrational spectra.

3 Vibrations and Thermal Properties

3.1 Heat Capacity

The heat capacity $C_v \approx C_p$ of a perfect crystal obeys Debye law $C_p(T) = C_D T$ at temperatures below $\sim 0.01 \theta_D$, where θ_D is the Debye temperature and $C_D \propto \theta_D^{-3}$ can be calculated from the sound velocities and the atomic density. At higher temperatures, C_p begins to probe the details of the atomic structure via the acoustic dispersion curves throughout the Brillouin zone and eventually the optic modes.

The measured heat capacity of α -quartz nicely illustrates this point. Below 5 K, C_p/T^3 almost perfectly matches the expected Debye value whereas the upturn above 10 K is fully described by the curvature of the acoustic phonon branches. In α -cristobalite, the SiO₂ polymorph whose density is close to that of the glass, C_p/T^3 reaches its constant Debye value only below 2 K, in agreement with its lower atomic density. Giving rise to a large bump around 13 K, the very steep increase at higher temperature is mostly related to the rapid flattening of the transverse acoustic branches in the $\langle 110 \rangle$ direction [4, 5]. Because a given vibrational mode contributes to the heat capacity according to its relative weight in the vibrational density of states, the intense Raman active zone center mode of α -cristobalite around 50 cm⁻¹ [6], for example, enhances C_p from 15 K, just above the maximum of C_p/T^3 .

In contrast, the heat capacity of ν -SiO₂ does not conform to Debye model. Its larger value at 2 K indicates extra modes at low frequencies. Close to 0 K, part of this excess is due to an almost linear contribution proportional to temperature, which is associated with tunneling states [7–9], whose discussion is beyond the scope of this chapter. Subtracting this feature (Figure 2a) still leaves an excess over the Debye prediction. In agreement with their analogous local order and atomic packing, ν -SiO₂ and cristobalite display similar peaks in $C_p(T)/T^3$ and reduced density of states $g(\Omega)/\Omega^2$. Such common features early indicated [4] that low-energy peaks are not a peculiarity of glasses [10, 11] although they do not necessarily imply a common origin for both kinds of phases. The heat capacity of cristobalite is, for instance, completely understood in terms of phonon-branch dispersion. In contrast, the linear dispersion of sound waves up to at least 440 GHz [3] in ν -SiO₂ gives a constant Debye value up to ~5.5 K (dashed line in Figure 2a) which is inconsistent

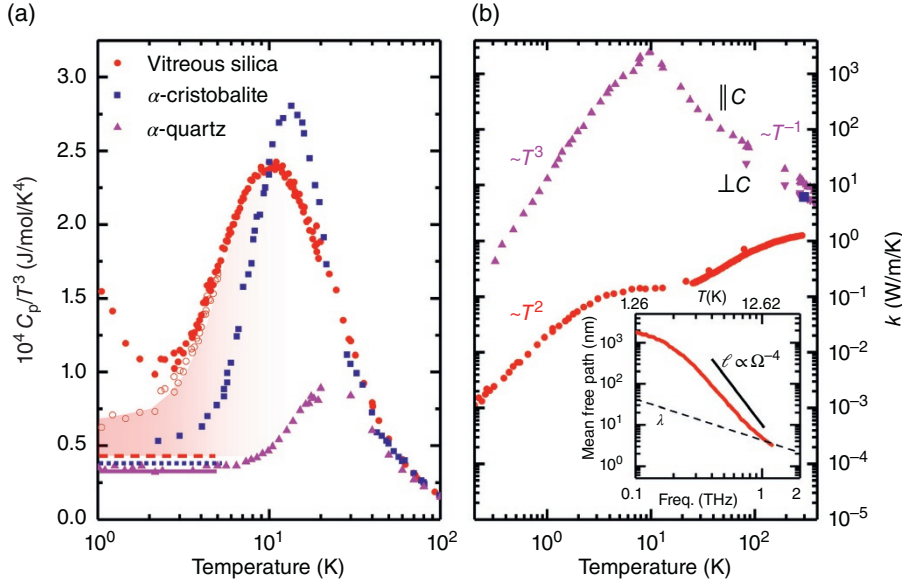


Figure 2 Low-temperature thermal properties of SiO₂ phases. (a) Low-temperature heat capacity of vitreous silica, α -cristobalite, and α -quartz in plots of C_p/T^3 against T . Horizontal lines: Debye constants (dashed, dotted, and full line, respectively). Open circles: C_p/T^3 of vitreous silica without the two-level system contribution. (b) Thermal conductivity of the same polymorphs. Inset: frequency dependence of the mean free path in vitreous silica in the dominant-phonon approximation.

with both the position and width of the peak in $C_p(T)/T^3$. One must assume instead a $g(\Omega) \propto \Omega^4$ relationship on top of the Debye contribution [7]. Such an Ω^4 dependence of the density of states is an ubiquitous feature in disordered systems [12]. But whether the excess above the Debye expectation at temperature below the maximum in C_p/T^3 (shaded area in Figure 2a) is a manifestation of disorder and, as such, is related to a strong scattering of the acoustic phonons in glasses occurring at high frequencies is a central and still unsettled question. Only these vibrational excitations define the *boson-peak modes*, as will be further discussed in Section 6.

3.2 Thermal Conductivity

In dielectric crystals, significant scattering of acoustic phonons is reflected in the low-temperature thermal conductivity κ . With the standard kinetic equation for gases, one approximately describes the temperature dependence of κ by

$$\kappa = \frac{1}{3} C_v \nu l, \quad (4)$$

where C_v is the heat capacity per volume of the excitations providing the thermal transport, ν their velocity of propagation, and l their mean free path [13]. This expression is obviously valid only for propagating phonons, i.e. below 1–2 THz in glasses as discussed below in the same subsection. From ambient, κ increases with decreasing temperature through the increasing lifetimes of acoustic excitations. As there are fewer and fewer phonons, l increases as T^{-1} at high temperatures. The mean free path is of course limited by sample dimensions so that κ goes through a maximum, the *Casimir limit*, and then

decreases with the T^3 dependence of C_v at low temperatures as illustrated by the thermal conductivity of α -quartz along the c -axis (Figure 2b).

By contrast, the thermal conductivity of a dielectric glass material is much lower and has a markedly different temperature dependence. These features are illustrated by vitreous silica (Figure 2b) for which κ increases non-monotonously with increasing temperature with a remarkable plateau beginning just below the hump in C_p/T^3 . At very low temperatures, κ follows an approximate T^2 law instead of the T^3 dependence expected from the Debye approximation. According to a widely accepted interpretation, this initial T^2 rise is due to interactions between phonons and tunneling states, which reduce l in glasses [7–9].

The microscopic origin of the plateau around 3–15 K is in contrast a much more controversial issue. In early calculations, a very efficient phonon-scattering mechanism was assumed by a proportionality of l to at least Ω^{-4} [14], which suggested Rayleigh scattering from disorder in the glassy network. From Eq. (4), it is possible to estimate a mean value for $l(T)$ that can be recast in $l(\Omega)$ with the dominant phonon approximation $\hbar\Omega \sim 3.8 k_B T$ (Figure 2b). In the hypersound frequency range, i.e. below 100 GHz, $l(\omega)$ exceeds 1 μm so that it is much larger than the acoustic wavelength λ , confirming the assumption of propagation. In this range, resonant relaxation by tunneling states dominates acoustic attenuation below 1 K (Figure 2b, top x scale), yielding $l(\Omega) \propto \Omega^{-1}$. Above about 100 GHz, $l(\Omega)$ drops rapidly following an approximate Ω^{-4} trend. Near 1 THz, it becomes comparable to the acoustic wavelength λ , marking the Ioffe-Regel crossover from propagating plane-wave acoustic modes to diffuse excitations. Above the corresponding frequency Ω_{IR} , the wave vector loses

its meaning and the notion of phonon becomes ill-defined. Sound waves do not propagate and can no longer transfer energy. The dominant phonon approximation certainly breaks down as well in this range. Only recently has this frequency region become available for coherent spectroscopy of acoustic phonons. At higher temperatures, κ rises again and eventually saturates at around 1 W/m/K. As heat transport can no longer be mediated by propagating sound waves, it is generally admitted that κ is governed here by diffusion mechanisms [15, 16].

Finally, the room-temperature conductivity of α -cristobalite of ~ 6 W/m/K (Figure 2b) is close to the value obtained in the direction normal to the c -axis in α -quartz and much higher than the ~ 1 W/m/K reported for ν -SiO₂. This feature suggests that the temperature dependence of the thermal conductivity of α -cristobalite is essentially governed by anharmonic processes and follows the expected crystalline increase up to the Casimir limit when the temperature is lowered. Hence, the very rapid flattening of the dispersion curves of the acoustic branches in the $\langle 110 \rangle$ direction, which causes the hump in C_p/T^3 , is by no mean sufficient in itself to produce a plateau in κ around 10 K.

4 Inelastic Spectroscopy in Glasses

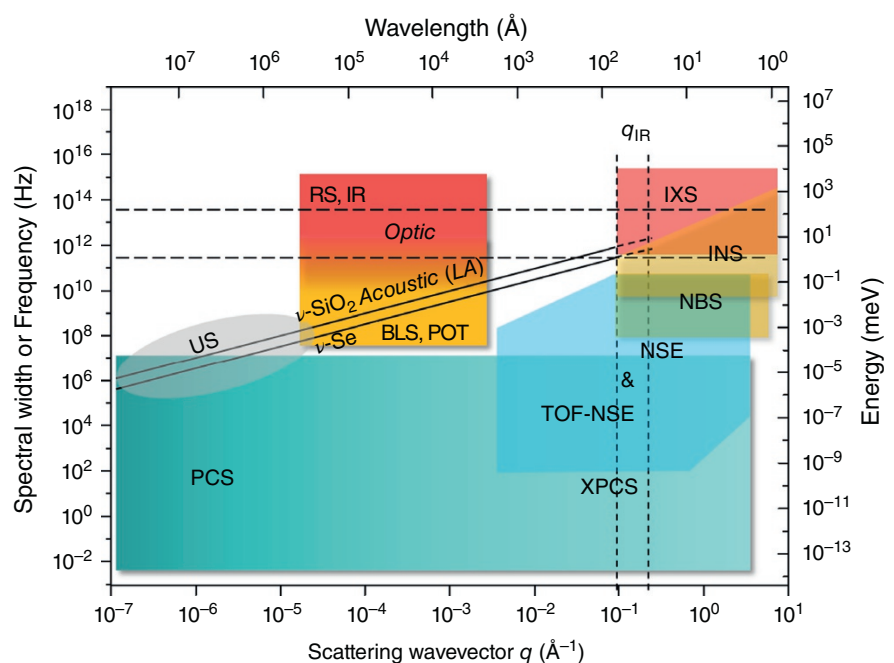
4.1 Dispersion Diagram and Experimental Techniques

The dispersion curves of the longitudinal phonons of vitreous silica and amorphous selenium, in the region where

they are plane waves, illustrate the variety of techniques used to study atomic excitations in disordered systems (Figure 3). The frequency range of network optic modes (typically between a few THz and ~ 2000 THz) is delineated by horizontal dashed lines whereas the boson peak stands on the low-frequency limit of that region (~ 0.5 – 3 THz). The longitudinal acoustic branch of vitreous silica has, for instance, been widely investigated by inelastic X-ray scattering (IXS), whereas ν -Se is one of the few examples where longitudinal sound velocity is sufficiently low to be accessible by inelastic neutron scattering (INS).

Depending on their frequency and scattering wave vector, some of the techniques displayed in Figure 3 are sensitive to relaxation only (X-ray photon correlation spectroscopy [XPCS], photon correlation spectroscopy [PCS], and neutron spin echo [NSE]), others to both relaxation and vibrations (ultrasonics [US], Brillouin light scattering [BLS], picosecond optical technique [POT], Raman scattering [RS], IXS, INS, and neutron backscattering [NBS]) whereas the scattering vector $\mathbf{q}$ is not defined for infrared absorption (IR) and US, which do not involve scattering. Much of the dispersion diagram is nowadays experimentally accessible except in the domain between 10^{-1} and $\sim 2 \times 10^{-3} \text{ \AA}^{-1}$ located at the limit of the Ioffe-Regel crossover region, defined by q_{IR} (Section 5.2). Owing to kinematic conditions, INS is not a technique of choice for such experiments, at least in structural glasses of rather high sound velocities. Close to $q = 0$, it is of course not possible to measure sound waves whose velocities are larger than those of the incident neutrons. Accordingly, the high-frequency limit of INS in Figure 3 roughly corresponds to the highest

Figure 3 Dispersion of longitudinal acoustic phonons in vitreous silica ($v_{\text{LA}} = 5960$ m/s) and selenium ($v_{\text{LA}} \cong 1800$ m/s) and relevant ranges of the scattering techniques probing atomic excitations in disordered materials: ultrasonics (US), Brillouin light scattering (BLS), Raman scattering (RS), picosecond optical technique (POT), infrared absorption (IR), inelastic neutron scattering (INS), inelastic X-ray scattering (IXS), neutron spin echo (NSE), neutron backscattering (NBS), photon correlation spectroscopy (PCS), and X-ray photon correlation spectroscopy (XPCS). The frequency domain of optic vibrations in network glasses is delineated by horizontal dashed lines.



neutron velocities enabling measurements down to $q \sim 0.1 \text{ \AA}^{-1}$. Another drawback of INS and IXS is their inability to probe transverse acoustic phonons close to $q = 0$.

4.2 Scattering Intensity

The intensity $I(\mathbf{q}, \omega)$ of an incident radiation scattered by a material is proportional to the space and time Fourier transform of the correlation function of the physical quantity (let us call it A), which couples to the incoming radiation [17]:

$$I(\mathbf{q}, \omega) \propto FT \left\{ \int_V \int_t A(\mathbf{r}, t) A(\mathbf{r} + \mathbf{r}', t + t') dt d\mathbf{r} \right\} \quad (5)$$

$$= C(A) \cdot S(\mathbf{q}, \omega).$$

For X-ray, neutron, and light scattering, A stands for the electronic density ρ_e , the coherence length b , and the dielectric susceptibility χ , respectively, and the function $C(A)$ expresses the selection rules of the scattering experiment. It depends on the strength of the coupling of the incident radiation to a vibration and, therefore, modulates the intensity of its spectral shape given by $S(\mathbf{q}, \omega)$. For light scattering, the susceptibility χ can be expressed in terms of the polarizability tensor $\bar{\alpha}$, the hyper-polarizability tensor $\bar{\beta}$, or the photo-elastic tensor $\bar{p}$, giving rise to Raman, hyper-Raman, and Brillouin processes. Neutron scattering is sensitive to all vibrations and enable measuring the phonon dispersion curves over a large $(\mathbf{q}, \omega)$ range. The vibrational density of states is given by the normalized integral over all $\mathbf{q}$ -values and yields $g(\omega)$. In neutron scattering studies, however, the latter is modulated by the coherent length of the atoms so that it remains an approximate quantity.

However, structural disorder prevents a general theory from being formulated to describe vibrational selection rules hidden in the expression of $C(A)$ in glasses, analogous to the role of group theory played for crystals and molecules. This is one of the main reasons why the description of atomic vibrations is hardly accessible. Another limitation is the spatial localization of the modes described in Section 4.3.

4.3 Coherent and Incoherent Scattering

In disordered media, a very important consequence of the spatial localization of extended waves is a loss of coherence of the scattering process due to the ill-defined nature of the wave vector $\mathbf{Q}$ of the vibration. But the momentum keeps conserved when modes are characterized by a

spatial extension larger than the probed wavelength, e.g. acoustic and optic phonons in crystals

$$\mathbf{Q} = \mathbf{q} = \pm (\mathbf{k}_i - \mathbf{k}_s). \quad (6)$$

Only the vibrations whose wave vectors $\mathbf{Q}$ match those of the experiments $\mathbf{q} = \pm(\mathbf{k}_i - \mathbf{k}_s)$ will then be active for a given scattering geometry. Hence, one observes that understanding selection rules requires to distinguish the frequency and wave vector of the vibration $(\Omega, \mathbf{Q})$ from that accessible by the instrument $(\omega, \mathbf{q})$.

The other extreme situation corresponds to non-propagating vibrations of fully localized molecular motions as observed in liquids or gases. A perfect localization in real space leads to an infinite spectral broadening of Q , $\Delta Q \rightarrow \infty$, in the Fourier space. Hence, $\mathbf{Q}$ is not a relevant physical quantity and the vibration scatters at every $\mathbf{q}$ value.

For the intermediate situation of quasi-localized vibrations, the coherence length of the mode – if it is sufficiently short – may induce a wave vector spectral broadening ΔQ (horizontal lines in Figure 1a). In that case, *the contribution at ω in the vibrational spectrum is the sum over all modes of frequency $\Omega = \omega$ having a wavevector spectral component Q matching the scattering wave-vector q of the experiment.* The above conclusion holds true in glasses for optic modes as well as for short-wavelength acoustic waves since the latter progressively transform into quasi-localized vibrating entities at high frequencies (cf. Section 2).

Another way to address the propagation of acoustic phonons in amorphous solids is to consider plane waves propagating in a mechanically inhomogeneous medium [18] where χ depends on position. The disorder induces a spatial modulation of the photoelastic constants, resulting in distorted acoustic waves whose coherence length is limited by local elastic inhomogeneities, as in the model developed in Section 2. A full treatment shows that the light-scattering spectrum consists of the usual Brillouin peaks and a background rising as ω^2 originating from the incoherent contribution induced by these local heterogeneities.

5 Vibrational Spectra

5.1 Optic Modes in the Glass Formers SiO_2 and B_2O_3

Incoherent scattering process combines with structural disorder to produce broad bands in the Raman and infrared spectra. If the glass has a short-range structure similar to that of a crystalline counterpart, its vibrational spectrum will generally represent a smeared-out version of that of the crystal. For example, the similarities

between vitreous silica and its crystalline counterparts are striking (Figure 4).

The lack of long-range order prevents vibrations in glasses from being described in a unique way. A first possibility is to consider the atomic displacements (eigenmodes) of an elementary structural unit such as the

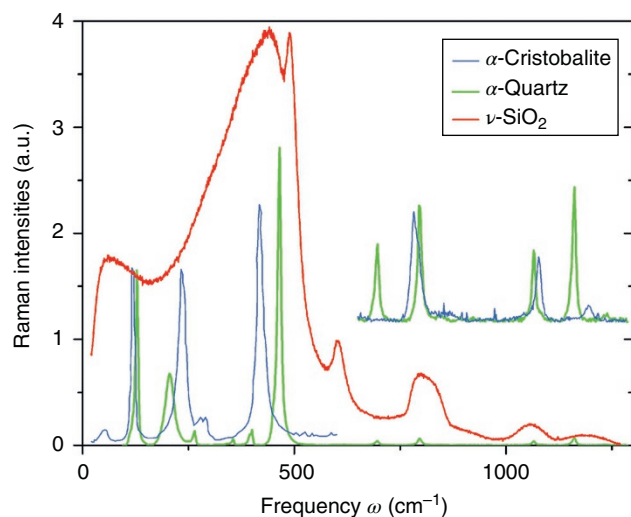
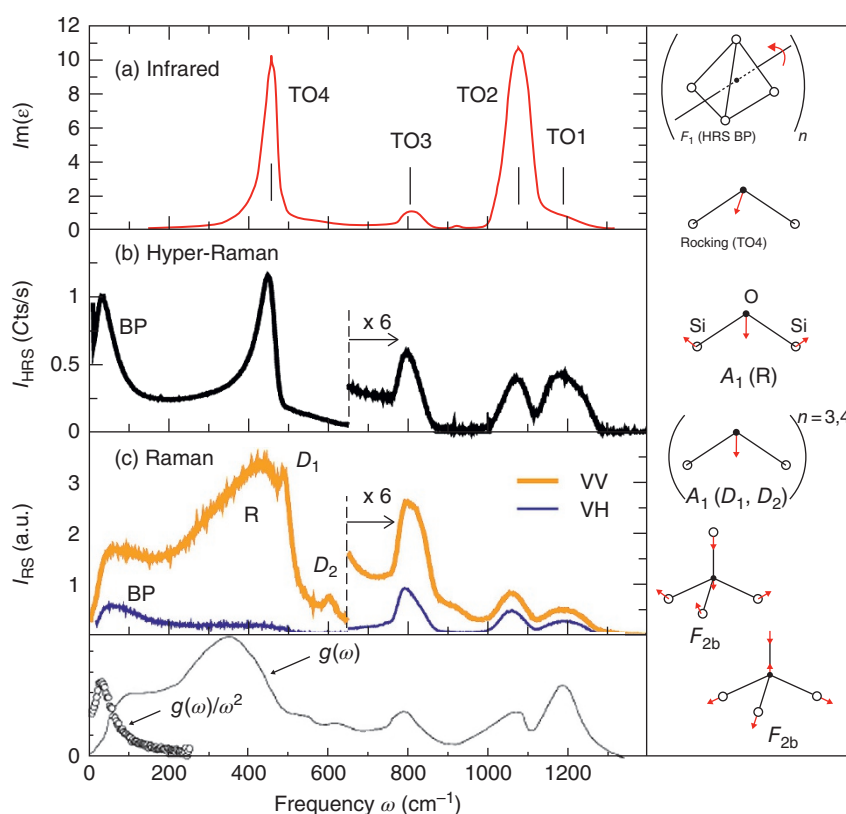


Figure 4 Raman spectra of ν -SiO₂, α -quartz, and polycrystalline α -cristobalite.

SiO₄ tetrahedron of T_d -symmetry or the Si–O–Si bridge of C_{2v} -symmetry in ν -SiO₂, and the BO₃ triangle of D_{3h} -symmetry or the B–O–B bridge in ν -B₂O₃. A second possibility is to define rocking, bending, and stretching motions of N–O–N units, where N=Si, B, Ge, etc. A pure bending modulates only the N–O–N bond angle whereas a pure stretching modifies the N–O bond length. Finally, numerical simulations often project displacements over three orthogonal axes also defined as bending, stretching, and rocking axes. The first one is perpendicular to the N–O–N plane, the second is parallel to the N–O–N bisector, and the third is parallel to the N–N direction. In that case, bending and stretching are not pure vibrational modes. These definitions are not unequivocal, however, so that they can foster confusion in mode assignments. Owing to network connectivity, the spectral responses generally involve several structural units, which further complicates the description. Although some of the conclusions are still discussed, atomic displacements are tentatively summarized hereafter for the main glass formers.

For ν -SiO₂ and ν -B₂O₃, the differences between the IR, Raman, and hyper-Raman spectra (Figures 5 and 6) indicate that selection rules do apply in glasses with sufficiently well-defined local structures. The three polar modes TO1, TO2, and TO3 in ν -SiO₂ are, for example,

Figure 5 Vibrational spectroscopy of ν -SiO₂ and atomic displacements for the main modes [19–21]. From top to bottom: infrared absorption, hyper-Raman scattering, Raman scattering, and vibrational density of states derived from neutron scattering [22]. N.B. F_1 vibrations seen in HRS are not the only ones participating in the boson peak.



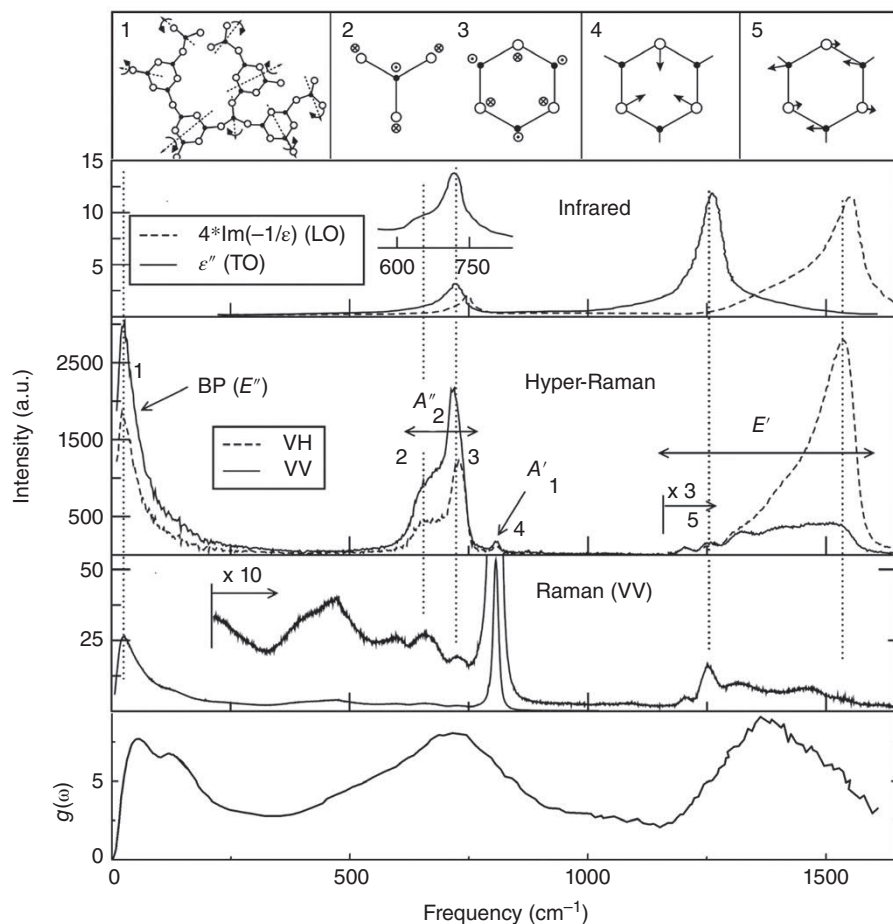


Figure 6 Vibrational spectroscopy of ν -B₂O₃ and atomic displacements for the main modes [19–21]. From top to bottom: infrared absorption, hyper-Raman scattering, Raman scattering, and vibrational density of states derived from neutron scattering [22]. N.B.: F_1 vibrations seen in HRS are not the only ones participating in the boson peak.

active in IR, Raman, and hyper-Raman, in agreement with either the C_{2v} - or T_d -symmetry selection rules. Within the T_d point group, F_2 -symmetry stretching motions of SiO₄ tetrahedra (F_{2s}) contribute preferentially to TO1 and TO2, whereas F_2 -symmetry bending ones (F_{2b}) dominate in TO3 [20]. Since the Raman inactivity of TO4 cannot be accounted for by any of the internal vibrations proposed by the two structural models, this mode rather represents highly cooperative motions involving rocking of the oxygen atoms [21, 23] in the Si–O–Si bridges the weak value of the depolarization ratio (I_{VH}/I_{VV}) of the Raman R , D_1 , and D_2 bands are compatible with A_1 -bending of the Si–O–Si bridges of C_{2v} -symmetry. The displacements are in phase in the three- and four-membered ring (Si–O–Si)_{*n*} planar structures ($n = 3$ and 4 , respectively), and are commonly ascribed to breathing modes. Such motions induce very weak dipolar fluctuations and are, therefore, almost inactive in IR and hyper-Raman scattering (HRS). Likewise, in the vibrational spectrum of ν -B₂O₃ (Figure 6), the atomic displacements proposed are compatible with the molecular selection rules of the D_{3h} -symmetry group of BO₃ triangles and B₃O₆ boroxol rings.

Although very powerful, vibrational techniques do not lend themselves to quantitative structural estimates. Even though numerical simulations are proving valuable in this respect, thanks to calculations of the coupling-to-light coefficients $C(A)$ in Eq. (5) or to NMR calibrations, the main asset of inelastic spectroscopies remains their ability to derive information that may be difficult or even impossible to obtain with conventional structural techniques. For example, three- and four-membered rings represent only one per 670 and 550 SiO₂ units, respectively [24]. These proportions are much too low to be detected in a diffraction experiment, but high enough to produce the narrow D_1 and D_2 Raman bands. Whereas the broad R -band probes the Si–O–Si angle distribution [22, 25], the high-frequency feature depends on the fraction of Q^n -species in binary or more complex silicates. The role of modifier, charge compensator, or glass former played by other cations can also be investigated. In ν -B₂O₃, structural information accessible by vibrational techniques concerns, for instance, the fraction of boroxol rings B₃O₆ and the ratio of BO₃-triangles and BO₄-tetrahedra in binary glasses (Chapters 2.8 and 7.6).

5.2 Acoustic Excitations

At large wavelength, i.e. in the continuum limit, acoustic waves propagate in glasses as they do in crystals. Almost nondispersive sound waves have been indeed measured at low frequencies with ultrasonic (MHz) Brillouin scattering (GHz) or picosecond optical pump-and-probe (100 GHz) experiments. At these frequencies, quasi-plane waves do propagate but with higher attenuation rates than generally found in crystalline solids. The anharmonicity of thermal atomic vibrations causes the attenuation of sound waves in crystals [26] and is in addition reflected in the temperature dependence of the sound velocities or in thermal expansion. The same mechanism is also present in glasses, but it coexists with other damping processes that are mostly specific to them.

At low frequencies, the energy mean free path of acoustic phonons is limited by resonant interactions with tunneling states at low temperatures and by thermally activated relaxation at higher temperatures, both leading to $l^{-1} \propto \omega$ (Figure 7a). The latter mechanism is empirically described by the relaxation of group of atoms or “defects” between two or more equilibrium positions [27, 28]. At hypersonic frequencies, anharmonic processes coexist with thermally activated relaxation to drive a smooth transition from a $l^{-1} \propto \omega$ law to a $l^{-1} \propto \omega^2$ trend from low to high temperatures as clearly observed above GHz frequencies (Figure 7a).

The combination of these mechanisms thus results in complex variations of $l^{-1}(\omega, T)$, which strongly depend on glass composition. Finally, very short-wavelength sound waves experience a disorder-induced strong scattering regime, which dominates above 0.1–0.2 THz, depending on temperature and on the efficiency of the other damping mechanisms. The dramatic increase of $l^{-1}(\omega)$ rapidly produces the Ioffe-Regel crossover at the frequency $\omega_{\text{IR}}/2\pi$ (Figure 7a). Such a rapid decrease of the mean free path is actually the trend required to produce the aforementioned plateau in $\kappa(T)$ around 10 K.

With techniques ranging from Brillouin to IXS, it has become possible to study longitudinal acoustic excitations just below the IR crossover. In two favorable cases [29, 30], detailed measurements have revealed the existence of a very rapid increase of the Brillouin linewidth $\Gamma = l^{-1}v_L$, where v_L is the longitudinal sound velocity as illustrated by lithium diborate glass $[\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$ at 573 K (Figure 7b, inset). In the Brillouin spectrum taken at the smallest usable Q , the fitted elastic peaks have been subtracted from both the data and the fit to make the inelastic parts and their damped harmonic oscillator components apparent. At this low- q value, the Brillouin width is almost entirely instrumental, whereas it contains a real and large broadening in the bottom inset. At that point, the lineshape of the damped harmonic oscillator begins

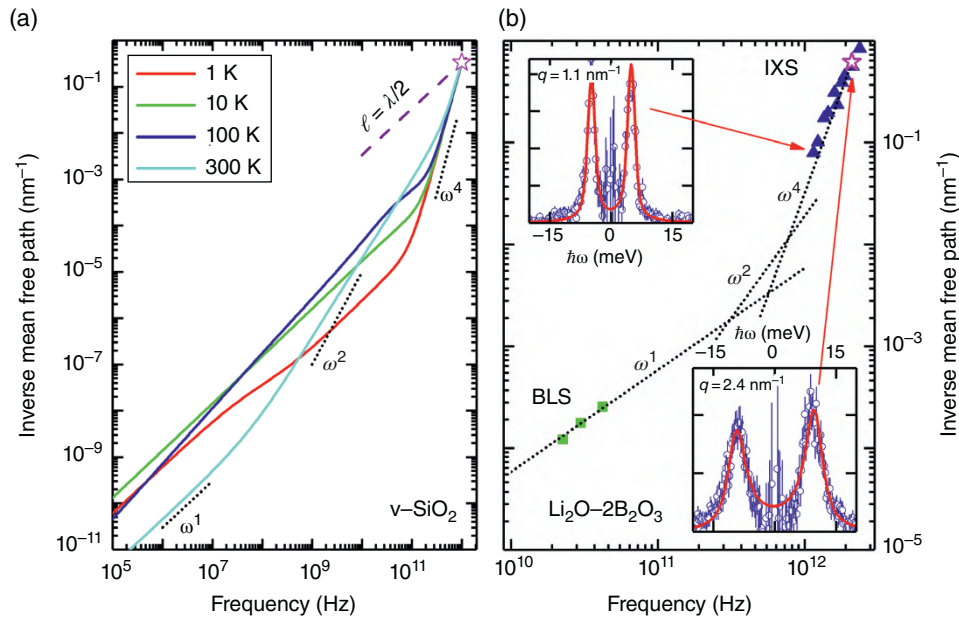


Figure 7 Inverse mean free path $l^{-1}(\omega, T)$ of longitudinal acoustic excitations in glasses. (a) For $v\text{-SiO}_2$: curves calculated with four damping mechanisms, namely, interactions with tunneling states, thermally activated relaxation, anharmonicity, and Rayleigh scattering at high frequency, which leads to the Ioffe-Regel crossover at ~ 1 THz (star). (b) For lithium diborate glass as measured at 573 K with BLS (green squares) and IXS (filled triangles). Dotted lines referred to the different damping processes: thermally activated relaxation plus lithium diffusion at GHz frequencies, anharmonicity around 0.5 THz, and Rayleigh scattering at THz frequencies. IR crossover at ~ 2.4 THz (star). Inset: dramatic increase of the Brillouin linewidth in IXS spectra in the IR crossover between $q = 1.1$ and 2.4 nm^{-1} .

to deviate increasingly from the measured signal. The reciprocal of the energy mean free path corresponding to the Brillouin linewidths from all the measured IXS spectra is reported in the main graph of Figure 7b.

Following a ω^4 trend, the dramatic increase of l^{-1} is clearly evidenced over a decade. At $q = q_{\text{IR}} = 2.4 \text{ nm}^{-1}$, the Brillouin linewidth reaches one-third of the Brillouin frequency, which is the Ioffe-Regel criterion. The IXS spectra measured at higher q values are inconsistent with a single damped-harmonic oscillator response, demonstrating that this approximation is no longer valid, thus marking the end of acoustic plane waves at q_{IR} in this glass. In Brillouin light-scattering experiments made at the same temperature (Figure 7b), the l^{-1} values obtained also show that damping in this (ω, T) region is dominated by thermally activated relaxation processes and lithium diffusion, leading to an approximate $l^{-1} \propto \omega$ dependence, in agreement with ultrasonic experiments. From the temperature variation of the sound velocity, an estimate of the anharmonicity contribution at 573 K ($l_{\text{anh}}^{-1} \propto \omega^2$ in Figure 7b) shows that this mechanism should dominate in a narrow frequency range around the crossover between ω^1 and ω^4 trends. More recently, similar IXS measurements made on ν -SiO₂ and glycerol [C₃H₈O₃] have also indicated such a dramatic increase of the reciprocal of the mean free path of longitudinal acoustic excitations at THz frequencies.

The results obtained for a densified ν -SiO₂ and then on lithium diborate glass have represented the first experimental evidence for the existence of a Rayleigh-type scattering mechanism of acoustic phonons in glasses producing an Ioffe-Regel crossover at some large acoustic wavelengths. The observation of both phenomena firmly demonstrated that the plane-wave approximation has already lost all validity at an intermediate scale, i.e. at about 1–3 nm depending on the glass. The observed crossover from propagating to diffusing sound waves has also offered a natural explanation for the anomalous low-temperature plateau in thermal conductivity. In several glasses investigated so far, ω_{IR} is close to the boson-peak frequency ω_{BP} , suggesting a direct relationship between both quantities. The correspondence is not one to one, however, as ω_{IR} remains at or above ω_{BP} . It is believed that the boson-peak frequency actually corresponds to the Ioffe-Regel crossover frequency for the transverse acoustic excitations in all glasses, but no experimental data have demonstrated the validity of this statement yet.

6 The Boson Peak

The excess of vibrational modes in the reduced vibrational density of states $g(\omega)/\omega^2$ translates into a broad and asymmetric band at frequencies between 0.5 and 3

THz in Raman or infrared spectra, corresponding approximately to the end of the acoustic branches. Vibrations of different origins are likely participating in that frequency region and should be separated into glass-specific vibrations (*boson-peak modes*) and crystalline-like vibrations (*non-boson-peak modes*). Many attempts have been made to relate the boson peak, e.g. to the medium-range order [31], the crystalline phases [11], or the macroscopic properties [32]. This section will focus on the origin of the vibrations underlying this excess of modes.

6.1 Oxide Glasses

In quartz, a very important vibration is the soft mode associated with the structural α – β instability at 846 K whose displacements have been interpreted as librations of SiO₄ tetrahedra. Its temperature dependence has been measured by neutron scattering (Figure 8b) and its frequency extrapolates to $\sim 36 \text{ cm}^{-1}$ at $T_g \sim 1600 \text{ K}$, i.e. to the frequency of the maximum of $g(\omega)/\omega^2$ measured by INS (Figure 8c). Librations of rigid units are also soft

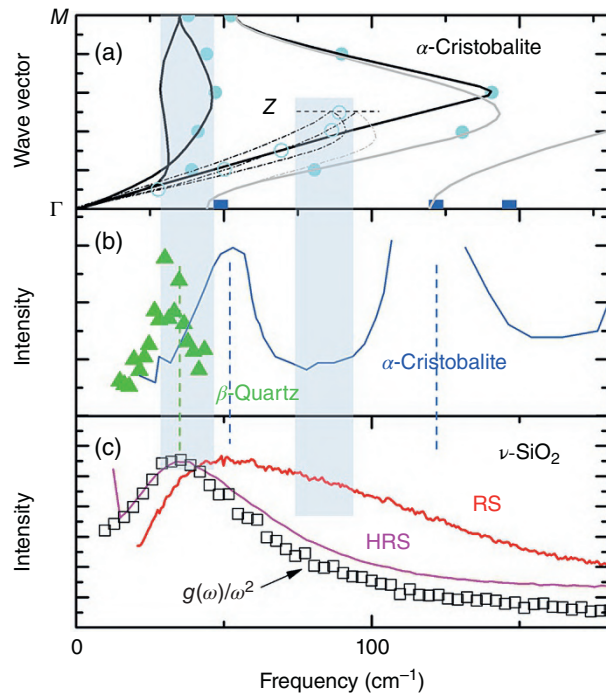


Figure 8 Vibrational excitations in ν -SiO₂. (a) Dispersion curve of acoustic modes and low-lying optic branches along the $\Gamma \rightarrow M$ (plain lines) and $\Gamma \rightarrow Z$ (dot dashed lines) directions of the Brillouin zone; squares Raman data. (b) Raman spectra of α -cristobalite and neutron spectra of the soft mode of β -quartz at 1250 K whose position at T_g is indicated by the dashed line at around 36 cm^{-1} . (c) Spectroscopic signatures of the boson peak; possible vibrational contributions indicated by shadowed regions and the vertical dashed lines.

vibrations in β -cristobalite but are located at the zone boundary of a transverse acoustic branch. These low-frequency excitations have been identified as *rigid unit modes* [33], i.e. external modes combining librations and translations of rigid elementary units. These units associate with weak interunit restoring forces in the glass and therefore vibrate at low frequency.

Similarly, INS, hyper-Raman, as well as numerical simulations have highlighted the presence of librations of rigid SiO_4 (F_1 -symmetry displacements in Figure 5) at boson-peak frequencies in vitreous silica [34, 35]. Librations also participate at boson-peak frequencies in pure boron oxide (Figure 6) but with a lower weight than in ν - SiO_2 . In this respect, silica is probably a peculiar system since librations are soft modes of the crystalline polymorphs, which to our knowledge is not the case for boron oxide. In connected networks, librations couple with translations of rigid units and hybridize with transverse and longitudinal acoustic phonons of similar frequency. This source of scattering combines with the strong scattering process of sound waves close to the Ioffe-Regel crossover frequency (shadowed regions in Figure 8a–c) to build up the reservoir of *boson-peak modes*. The loss of the Brillouin zone combined with the localization of the plane waves in the glass makes identification of these vibrations as acoustic- or optic-like useless. Owing to the different nature of these modes, the boson peak manifests itself in a way specific to the spectroscopic technique used, leading to differences in neutron, Raman, hyper-Raman, and infrared responses. What matters first and foremost is that these excitations relate to the structural disorder of the glass and to the plateau of the thermal conductivity.

Crystalline-like modes may also contribute at frequencies beyond that of the boson peak such as the Raman modes at ~ 50 and $\sim 120 \text{ cm}^{-1}$ in α -cristobalite (Figure 8b) [36] or cation modes in soda-lime-silicate glasses [37]. Indeed, the vibrational density of states $g(\omega)$ of ν - SiO_2 below 300 cm^{-1} (as well as its Raman spectra) is very complex, pointing to numerous low-frequency optic vibrations (Figure 5). Conversely, that of B_2O_3 looks like Van-Hove singularities of transverse and longitudinal acoustic branches (Figure 6) emphasizing thereby a much weaker contribution from *crystalline-like* optic modes.

6.2 Other Glasses

The picture is even more complicated in molecular glasses (e.g. glycerol, ortho-terphenyl) where a large number of intramolecular and reorientational motions are likely to contribute at low frequency, leading to a great complexity in both vibrational responses and structural relaxation (Chapter 8.6). Hence, these systems generally do not represent good model systems for studying the boson peak.

Metallic glasses may in contrast prove useful in this respect. The simplest ones can be usually described as chemically and positionally disordered dense-packed structures without orientational interactions or intramolecular processes (Chapter 7.10). Consistent with the Lennard-Jones interacting-sphere model, the excess of low-frequency modes in C_p between ~ 10 and 30 K is then often composed of purely harmonic vibrations, i.e. of Einstein modes corresponding to local excitations of loose atoms in the glassy structure. Unfortunately, electronic and atomic properties often mix in metallic glasses, which may confuse the description of the boson peak and thermal properties. Electronic processes at impurity sites may, for example, contribute to localized excitations at boson-peak frequencies whereas thermal conductivity may also be dominated by electronic heat-transfer channels, which are much more efficient than atomic ones in conductors.

In the large family of non-insulating glasses, amorphous silicon (a -Si) is probably one of the simplest examples. Its crystalline counterpart (c -Si) has only one triply degenerate optic mode at $\omega = 520 \text{ cm}^{-1}$, which leads to an interesting situation where only acoustic branches contribute to the vibrational density of states below $\sim 350 \text{ cm}^{-1}$ (Figure 9a). The crystalline tetrahedral short-range order is preserved in the glassy state so that the densities of the two forms differ by 1.8% only. This structural similarity lends support to qualitative comparisons between vibrational properties. For example, the vibrational densities of states are similar below $\sim 350 \text{ cm}^{-1}$ with only a downshift of the band maxima in the glass, reflecting lower sound velocities (Figure 9b). Despite the absence of optic modes at low frequency, the Raman spectrum is not flat but displays broad structures that have been associated with both second-order processes on acoustic branches [38, 39] and disorder-induced scattering due to acoustic plane-wave destruction (Sections 2 and 5.2). The latter effect seems to be rather weak in a -Si, however, since it yields a moderate damping mechanism of the acoustic phonon branches, proportional to q^2 [16, 40], as compared with the very fast q^4 -law observed in network glasses. This probably explains why the Raman response is very similar to the $g(\omega)$ measured by INS (Figure 9b) [41].

As in crystalline silicon, C_p/T in a -Si varies without showing evidence for two-level systems at least down to 2 K [4, 42]. The weak damping regime of the acoustic phonons goes against the formation of a plateau in the thermal conductivity as well. Unfortunately, however, existing reports are controversial and firm experimental evidence is still lacking on that question. Finally, the Ioffe-Regel crossover frequency is upshifted toward the end of the transverse acoustic branch (Figure 9b) [16], which raises some doubts about its physical meaning.

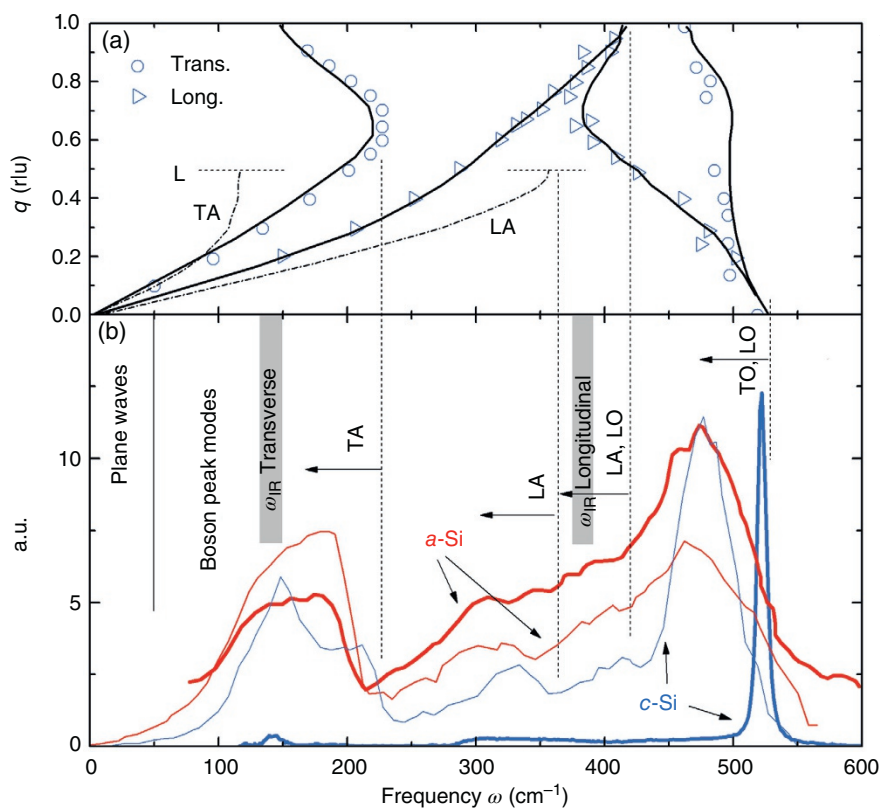


Figure 9 Vibrational excitations in crystalline and amorphous silicon. (a) Dispersion curves along the X (symbols and lines) and L (dot-dashed lines) directions of the crystal [38]; dispersion curves of acoustic phonons about 25% lower in the glass than in the crystal. (b) Vibrational density of states $g(\omega)$ (thin lines) [41] and Raman scattering spectra (bold lines) of amorphous silicon [37] and c-Si. Plane wave, boson-peak mode, and ω_{IR} transverse and longitudinal acoustic limits taken from [16].

In the current state of knowledge, the only reliable glass-specific vibrational feature of amorphous silicon is, therefore, the partial destruction of acoustic plane waves at large q (i.e. short wavelengths). Although moderate, this mechanism generates *boson-peak modes* at frequencies between the plane-wave regime and the Ioffe-Regel crossover at ω_{IR} .

7 Perspectives

Inelastic scattering selection rules in glasses are relaxed by local structural and mechanical disorder, yielding broad and asymmetric spectral responses. Unlike for crystals, there exists no well-established analytical theory of the atomic displacements that underlie the spectral responses. Analyses remain mostly phenomenological, except perhaps for simple glasses for which atomistic simulations nowadays provide a firmer theoretical foundation. Indeed, the nature of the vibrations in the main oxide glass formers, up to binary and to a lesser extent ternary systems, is relatively well understood. Extracting quantitative structural information, in particular from RS, remains a challenging issue.

Even more challenging is the nature of the boson peak. Its modes participate at low frequency in the vibrational

spectra of most disordered systems. These vibrating entities mostly originate from a renormalization and a redistribution of the modes of the acoustic branches due to the destruction of plane waves of nanometer wavelengths. They can eventually hybridize with low-lying optic vibrations (rigid-unit modes), such as the librations of rigid SiO_4 tetrahedra in silica or loose local atomic motion in Lennard-Jones-type metallic glasses. The purely acoustic-type damping mechanism, enhanced by the second one when relevant, induces a very fast decay of the mean free path of the acoustic phonons at THz frequency, as evidenced by IXS and numerical simulations. There follows a crossover from a propagative to a diffusive character of sound waves and offers a natural explanation of the low-temperature plateau of thermal conductivity.

These modes build up the boson-peak structure mostly below its maximum in $g(\omega)/\omega^2$ plots in Raman and INS spectra. At higher frequencies, this spectral response mixes with those of other mechanisms, such as incoherent scattering from high-frequency acoustic branches due to the loss of wave vector selection rules, direct scattering of low-lying optic branches, second- or higher-order RS processes, and possibly others. It is tempting to define the boson peak as arising from the sum of all the excitations that construct the broad feature at THz frequency in glass, as it is often done in literature. Here, we have

preferred to separate the *boson-peak modes* from the other scattering processes since the latter are related to spectroscopic considerations whereas the former accounts for solid-state properties specific to glasses. Current advances in numerical simulations have allowed the boson-peak modes at the origin of the plateau in κ to be identified in very few cases [16, 43]. Highlighting them over the other scattering channels in a scattering experiment probably constitutes one of the most challenging issues of the coming decades.

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3.5

Density of Amorphous Oxides

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1 Introduction

Density is a fundamental thermodynamic property, an essential characteristic of any condensed phase and one that is readily measured with great accuracy. The density of glassy and/or molten oxides is also of significant practical interest in a wide range of industrial and geological contexts. In the glassmaking and metallurgical industries, the difference in density between molten silicates and metals is the key to successful manufacture of everyday products such as float glass used in the construction and automobile industries, whereas, farther from home, the density of magmatic silicate liquids controls the time-scales of movement and the spatial distribution of crystals within the interiors of the Earth, Moon, and Mars.

In a little more detail, the density of amorphous oxides is a function of composition, temperature, and pressure. In the liquid state, temperature and/or compositional gradients can thus lead to density differences that are capable of driving material transport (i.e. convection), leading to mixing that may or may not be favorable for a given application. This link between large-scale material transport and liquid density highlights the critical importance of derivative properties such as thermal expansivity.

Temperature-dependent changes in density are also particularly critical when cooling a liquid across the glass transition. If the need to anneal a glass before cooling it down to room temperature has been known from time immemorial, it was understood only in the nineteenth century that the internal stresses to be eliminated in this

way originated from small changes in the local cooling rate throughout the glass piece (Chapter 3.7). Conversely, it was then realized that controlled generation of high local compressive stresses either by thermal or chemical means could be used to strengthen glass (Chapters 3.7 and 3.12). In the glassy state density continues to play a role, having an effect on optical properties such as refractive index and sound wave propagation. For example, chemical heterogeneities result in density differences that cause deformation of the optical path, a phenomenon generally observed in window panes produced before the float process was designed (Chapter 1.3).

Further to these general considerations, it must not be forgotten that the pressure dependence of the Gibbs free energy of a phase of constant composition is simply the volume. In other words, liquid volume (and thus density) has a direct influence on free energy and thus on phase equilibria, in particular on the variation of melting temperature as a function of pressure. One obvious application of this fact is that high-pressure melting of planetary interiors is critically sensitive to liquid volume and its pressure derivative, compressibility.

This brief introduction highlights a few of the implications of the density of amorphous materials. In the following, we will focus on a more detailed assessment of how volume is measured both at high and low temperature; how densities vary as a function of composition, temperature, and pressure; and how future work may lead to new breakthroughs in understanding variations in volume and/or result in novel practical applications. In addition to volume (V), the properties of interest here are the thermal expansivity $(\partial V/\partial T)_P$ and the isobaric thermal expansion coefficient $\alpha = 1/V(\partial V/\partial T)_P$ along with the isothermal and adiabatic compressibilities, $\beta_T = -1/V(\partial V/\partial P)_T$ and $\beta_s = -1/V(\partial V/\partial P)_S$, respectively.

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2 Measuring the Density of Amorphous Oxides

2.1 Theoretical Considerations

For a homogeneous liquid in internal thermodynamic equilibrium, the volume is uniquely defined at a given pressure and temperature (Figure 1). This also applies to the supercooled liquid state in the absence of crystals as long as the experimental timescale is longer than the structural relaxation time (Chapter 3.12). Because structural relaxation is a thermally activated process, with a more or less exponential temperature dependence, the transition from a fully relaxed liquid in internal equilibrium to an amorphous material whose structure is fixed (i.e. a glass) typically occurs over a restricted temperature range upon cooling.

This kinetic origin of the liquid-to-glass transition has the consequence that the temperature at which internal equilibrium of the liquid can no longer be maintained depends on cooling rate. Because the thermal expansion coefficient markedly decreases from the liquid to the glass state, the volume/density of a glass cannot be calculated from pressure, temperature, and composition alone, but also requires knowledge of the temperature–time path during cooling. Put another way, glass chips of the same composition can have different densities if they have been cooled at different rates (Chapters 3.8 and 10.11).

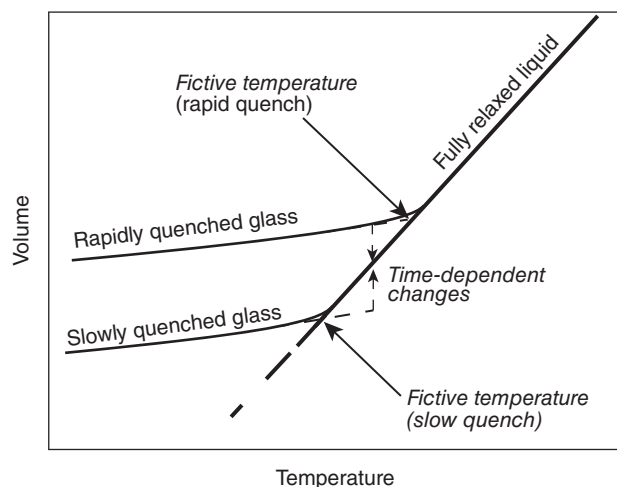


Figure 1 Volume variations in the glass transition range: contrast between the uniquely defined value of the supercooled liquid and the cooling-rate-dependent values of the glass. Limiting fictive temperature defined by the intersection of the extrapolated glass and liquid curves. Volume changes toward the equilibrium value associated with structural relaxation indicated by the thin dashed lines (after [1]).

2.2 Density of Amorphous Solids

Some of the earliest attempts to measure the density of amorphous oxides systematically were developed by the glassmaking industry well over 100 years ago with a simple but efficient technique with which a glass bead is immersed in a liquid whose temperature is varied until its point of neutral buoyancy is reached. If the density of the liquid is known as a function of temperature, then that of glass may be determined to better than 0.05%. Whereas this technique is well suited for extremely precise measurements of a sample whose density is approximately known, it is far less practical for an unknown sample since a given reference liquid only covers a small range of density.

For this reason, alternative methods have been developed, also typically based on Archimedes' principle, which states that a solid body immersed in a fluid is buoyed up by a force equal to the weight of the fluid displaced by the body. One may apply this principle to measure the density of amorphous solids (ρ_s) by weighing a glass chip in air and in a fluid of known density (ρ_l), such as toluene. The weight in air provides a measurement of the mass of the chip, whereas the difference between the weight in air and in the fluid is used to calculate the volume of the chip with

$$\rho_s = \frac{\rho_l w_a}{(w_a - w_l)}, \quad (1)$$

where w_a and w_l are the weights of the sample in air and in the immersing liquid, respectively. Such measurements present no particular difficulties, requiring only a high precision balance and a good control and measurement of temperature, because the density of the fluid bath depends on this parameter. It is good practice to check the density of a well-known standard such as sapphire before measuring the density of several glass chips. Under these conditions, errors lower than $\pm 0.0003 \text{ g/cm}^3$ can readily be obtained for glass chips of a few tens of milligrams.

2.3 Measurements in the Glass Transition Range

In the glass transition range, it is possible to study the properties of fully relaxed supercooled liquids that do not crystallize [1, 2]. However, the high temperatures and high viscosities of the liquids then prevent Archimede-based techniques from being used. One simple approach is to measure glass density as a function of temperature and extrapolate to the fictive temperature where the density of the glass and liquid are identical. In this way, a single volume (density)–temperature coordinate of the liquid can be defined, a data point that can be

combined with measurements made at superliquidus temperatures.

A more detailed knowledge of volume in this temperature range is also possible if one simply measures temperature-dependent length changes of fully relaxed liquids in the glass transition range. However, the temperature must be low enough for the viscosity of the sample to be sufficiently high that the sample does not collapse under its own weight, nor deform under the weight of the system used to measure length change. This constraint requires viscosities higher than $\sim 10^{11}$ Pa s. Given such high viscosities, care must be taken to ensure that the time spent at a given temperature is sufficiently long for the liquid to reach a fully relaxed state. Such measurements require excellent temperature stability and can last up to several days for a single measurement, but they provide direct and precise insight into volume changes over a temperature range of typically 50 °C [1, 2]. Furthermore, such measurements strikingly highlight the difference between the instantaneous elastic response of the sample to temperature change and the longer temperature-dependent viscous response that scales with structural relaxation time (Figure 2).

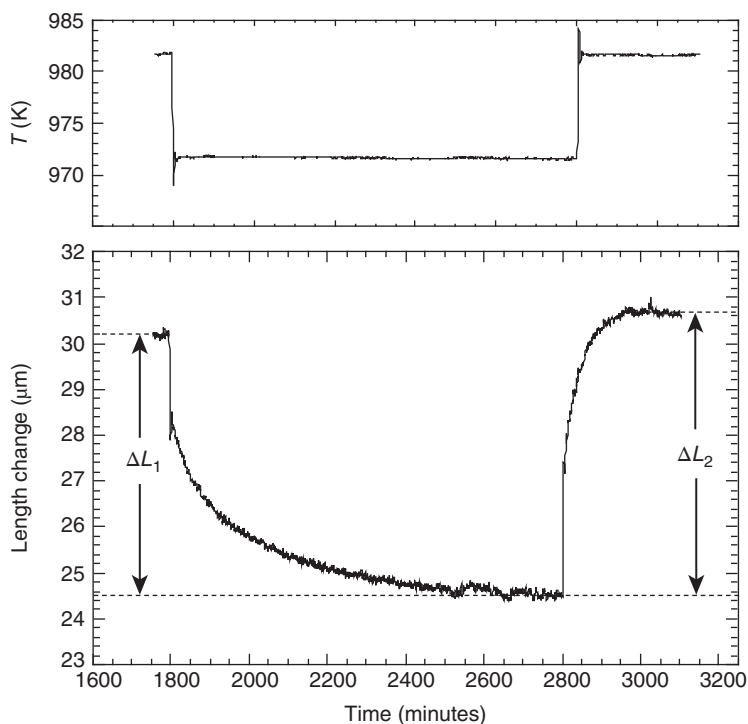
An alternative method for measuring the volume of a fully relaxed liquid at low temperature uses the equivalence of enthalpy and volume relaxation in the glass transition range that has been demonstrated for silicate, aluminosilicate, and borosilicate liquids [2]. In this case, when heating a glass to the fully relaxed liquid state,

the variation of the derivative property heat capacity ($\partial H/\partial T$) as a function of temperature should show the same normalized variations as expansivity ($\partial V/\partial T$). Given that heat capacity may be readily measured at all temperatures across the glass-to-liquid transition and that expansivity may be measured to temperatures at least as high as the peak associated with hysteresis, the expansivity of the relaxed liquid just above the glass transition can be inferred [3].

2.4 Measurements at Superliquidus Conditions

Superliquidus melts are typically of low viscosity, so Archimedes' principle can be used again to measure liquid density. In this case, the melt is held in an inert crucible (typically Pt or Pt/Rh) and an inert "bob" of known mass and density (and thus volume) is introduced into the molten oxide at high temperature [4]. The difference in weight of the bob measured in air and in the molten oxide provides a measure of the mass of molten oxide displaced. Knowing the volume of the bob, the density of the melt can thus be determined from Eq. (1). The difficulty associated with this sort of experiment resides in making stable measurements at the necessary high temperatures, typically in the range of 1200–1600 °C for molten silicates. Potential edge effects between the bob and the crucible and surface tension effects at the melt–air interface require the use of two bobs of different mass in order to provide robust determinations of liquid density. For this

Figure 2 Imposed variation of temperature (upper panel) and associated effect on length of a cylinder of supercooled $\text{CaMgSi}_2\text{O}_6$ liquid (lower panel). The variation in length of the sample clearly distinguishes the instantaneous (vibrational) and delayed (configurational) contributions to volume relaxation in response to a temperature change, in addition to illustrating the temperature dependence of relaxation time (after [1]). The total length change as a function of temperature may be used to quantify expansivity, this method providing a highly precise estimate of this parameter.



reason this technique is generally referred to as the *double-bob* Archimedean method. Under optimal conditions, inaccuracies as small as 0.2–0.3% in density are possible. Other techniques such as the maximum bubble-pressure method or use of falling spheres have uncertainties that are up to 10 times larger, so data acquired in those ways are not generally considered today.

For liquids melting at temperatures high enough that Pt equipment may no longer be used, crucibles and bobs can be made of other noble metals such as Ir, extending the possible temperature range to $\sim 1800^\circ\text{C}$. Above such temperatures it becomes difficult to find materials that are rigid enough to contain the melt while remaining inert. In this case containerless levitation techniques can now be employed. For example, a laser-heated sphere of known mass can be suspended on a jet of inert gas imaged in 3-D and its volume measured as a function of temperature. However, in light of the experimental difficulties associated with temperature control and measurement on the one hand and variations in the shape of the sample on the other, the inaccuracies of such measurements are at this moment three or four times higher than for the Archimedean techniques [5].

2.5 Compressibility and the Pressure Dependence of Density

The variations of volume with pressure are typically determined in one of two complementary ways. First of all, use may be made of the fact that the velocity of wave propagation in a liquid (v) is a function of density (ρ) and the adiabatic bulk modulus (K_s) according to the equation

$$K_s = \frac{1}{\beta_s} = \rho v^2. \quad (2)$$

It should be appreciated, however, that if the characteristic timescale of the wave (i.e. the inverse of its frequency) is shorter than the structural relaxation time of the liquid, then some fraction of energy may be transported by shear waves. In this case, the bulk modulus has contributions from both longitudinal modulus and shear modulus. It is thus essential to measure the speed of wave propagation over a wide range of frequencies to ensure that a constant value is determined, indicating that the bulk modulus is that of a fully relaxed liquid. For the case of sound waves in the kHz to MHz range, this constraint typically means studying liquids whose shear viscosity is less than 10 Pa s.

Use of ultrasound techniques to measure the compressibility of liquids dates back to the nineteenth century, but such techniques were dramatically improved by the advent of interferometry in the early twentieth century and then subsequently adapted in the mid-twentieth

century to the high-temperature measurements of molten oxides [6].

More recently the Brillouin scattering technique has been used to measure the compressibility of molten silicates up to temperatures exceeding 2300 K [7]. Because this technique employs hypersonic frequencies (a few tens of GHz), structural relaxation is negligible, and only the vibrational (glassy) contribution to compressibility is measured in this case. The difference between fully relaxed compressibilities measured using ultrasonic frequencies and the fully unrelaxed value determined using hypersonic frequencies can be used to derive the configurational contribution to compressibility [7]. Despite the constraints of high temperature, adiabatic moduli may be determined with these techniques to within 1%, allowing reasonable extrapolation of density around the chosen reference pressure (most conveniently 1 bar).

On the other hand, when pressure is much greater than 1 bar, a direct measurement of density is to be preferred to provide a well-constrained equation of state, including the pressure dependence of compressibility. In this respect, the most commonly employed experimental technique consists of bracketing the density of a high-pressure liquid relative to the known densities of minerals or metals such as boron nitride, platinum, graphite/diamond, or refractory olivine. In this case, a capsule containing the liquid of interest is placed within a piston-cylinder or multi-anvil device in which pressure may reach up to ~ 25 GPa. Two spheres of the solid whose equation of state is well known are added to the capsule, one at each extremity (i.e. top and bottom). After a sufficient time spent at high temperature and pressure, one determines whether the spheres sink or float in the liquid (thus the name sink/float technique). This assessment may be made based on *ex situ* techniques, that is to say, after quenching the sample and then determining if the spheres end up at the top or the bottom of the capsule [8]. Alternatively, with the advent of synchrotron facilities, it is now possible to observe the movement of a sphere within the liquid *in situ* at high pressure and temperature. Again, sinking and floating spheres indicate whether or not markers are denser than the melt.

With these techniques, the result of a given experiment does not provide a direct measurement of the density of the liquid, but rather an open-ended bracket. Precise determination of liquid density thus ideally requires a neutral buoyancy experiment bracketed by a sink and a float at slightly lower and higher pressures. Further complications include uncertainties in the equation of state of the density markers and potential chemical reaction between the markers and the liquid of interest. For all these reasons, high-pressure densities measured in this way typically have inaccuracies of several percent, which is minor relative to the 25–50% change in density that

typically occurs over pressure ranges of ~ 10 GPa [8]. In this pressure range, more refined *in situ* X-ray techniques with synchrotron radiation have recently been used to measure density from the absorption coefficients of the liquids and the compressibility from the structure factor q (cf. Chapter 2.2) [9].

At pressures higher than those accessible to the sink/float technique, liquid densities may be measured from shock-wave compression. In this technique a projectile is launched at variable velocity against a liquid sample held in an inert metallic capsule. From determination of the shock Hugoniot, that is to say, the covariation of shock and particle velocities in the sample, the pressure–volume coordinates of the sample during isentropic compression can be derived. The extreme conditions and elevated cost of the experiment, the short timescales involved (potentially leading to incompletely relaxed states), and the necessary presence of capsule materials in front of and behind the liquid sample make such measurements challenging, but densities can be measured with an imprecision on the order of 1% for pressures up to at least 250 GPa [10].

3 Measured Density Variations

3.1 Superliquidus Densities at 1 bar: Variations as a Function of Composition

The superliquidus volumes of the common network-forming oxides such as SiO_2 , B_2O_3 , P_2O_5 , and GeO_2 have all been determined, but these are not necessarily the easiest materials to investigate owing to their high liquidus temperatures and viscosities (e.g. SiO_2), their volatility (e.g. B_2O_3), or their corrosive nature (e.g. P_2O_5). Indeed, the direct measurement of the molar volume of pure liquid SiO_2 is so challenging that indirect measurements such as extrapolation of densities to pure SiO_2 from binary systems, use of the melting curve of cristobalite, and measurements on quenched glasses are preferred measures of the molar volume and expansivity for this oxide [11].

Since the 1950s, early systematic interest in the density of molten oxides was largely driven by the field of metallurgy, with the acquisition of data in many binary and ternary systems containing silica as the principal oxide, diluted by various network-modifying oxides, such as SiO_2 – Na_2O or SiO_2 – CaO (e.g. [4]). The densities measured in these simple systems demonstrate that for mole fractions of SiO_2 ranging from 0.35 to 0.85, molar volume is approximately a linear function of composition at fixed temperature. This observation indicates that in terms of volume, silicate liquids can be considered as ideal solutions (i.e. there is no excess molar volume associated with

mixing of different components), offering the possibility to construct simple predictive models for superliquidus density (e.g. [4, 12]). If the same is true at all temperatures and pressures, then to a first approximation the bulk density of complex liquids can be reconstructed from a set of partial molar volumes at reference conditions (V_i°), partial molar expansivities (dV_i/dT) and partial molar compressibilities (dV_i/dP), one for each oxide component.

$$V_{\text{liq}}(T, P, X_i) = \sum X_i \left[V_i^\circ + \frac{dV_i}{dT}(T - 1673) + \frac{dV_i}{dP}(P - 1) \right], \quad (3)$$

where $V_{\text{liq}}(T, P, X_i)$ is the molar volume of the liquid at temperature T (in K) and pressure P (in bars), and V_i° are the partial molar volumes at reference conditions of 1673 K and 1 bar.

In subsequent years, the earth science community spearheaded the acquisition of new data across a broad compositional range in multicomponent systems containing up to 10 different oxides, albeit still concentrated on liquids dominated by silica. This wealth of new high-quality data made it possible to refine the predictive models for superliquidus density, confirming that simple temperature-dependent partial molar volumes that are constant across wide compositional ranges are generally an excellent first-order approximation, both for aluminosilicate and borosilicate melts [13, 14; Table 1).

In detail, certain authors have highlighted deviations from ideality that are typically assumed to originate in one of two ways. First of all such nonidealities may represent an excess volume resulting from the interaction of two or more oxide components. Alternatively, a given oxide component may have more than one possible structural environment in the melt, each one having a different partial molar volume.

For the first case, pushing compositions to extremes can reveal the limits of the ideal mixing approximation. This is illustrated by measurements across the CaO – Al_2O_3 – SiO_2 ternary that include data for CaO -free, Al_2O_3 -free, and SiO_2 -free liquids [20]. However, even in this extreme case, a single excess volume term between CaO and SiO_2 is sufficient to rationalize all the data.

An illustration of the second case is provided by TiO_2 , an oxide component that has a partial molar volume in silicate melts that increases with the addition of alkalis (e.g. Figure 3a). This increase can be understood by the associated increase in the mean coordination number of Ti in the liquid (Figure 3b). Similar effects can also be found for expansivities, the thermal expansion of the TiO_2 component decreasing as alkali content increases [19].

The case of B_2O_3 is also of interest in this respect as boron occurs in both threefold and fourfold coordination in silicate and alumina-silicate melts, the relative

Table 1 Partial molar volumes, thermal expansions, and compressibilities of oxide components of silicate liquids.

	V_j^o _{1673K}	$(dV_j/dT)_{1\text{bar}}$	$(dV_j/dP)_{1673\text{K}}$	$[(dV_j/dP)]/dT$
	(cm ³ /mol)	(10 ⁻³ cm ³ /mol-K)	(10 ⁻⁴ cm ³ /mol-bar)	(10 ⁻⁷ cm ³ /mol-bar-K)
SiO ₂ ^a	26.90	0	-1.89	1.3
TiO ₂ ^{a,b}	23.16	7.24	-2.31	—
Al ₂ O ₃ ^a	37.11	2.62	-2.26	2.7
B ₂ O ₃ ^c	41.10	7.64	—	—
Fe ₂ O ₃ ^d	41.52	0	-2.53	3.1
FeO ^e	12.68	3.69	-0.6	-1.8
MgO ^a	11.45	2.62	0.27	-1.3
CaO ^a	16.57	2.92	0.34	-2.9
SrO ^f	20.45	3.1	—	—
BaO ^f	26.20	4.6	—	—
ZnO ^f	13.46	5.8	—	—
MnO ^f	14.13	2.1	—	—
NiO ^f	12.48	3.1	—	—
PbO ^f	25.71	4.1	—	—
Li ₂ O ^a	16.85	5.25	-1.02	-4.6
Na ₂ O ^a	28.78	7.41	-2.4	-6.6
K ₂ O ^a	45.84	11.91	-6.75	-14.5
Rb ₂ O ^f	54.22	33.2	—	—
Cs ₂ O ^f	68.33	48.8	—	—
P ₂ O ₅ ^g	64.50	—	—	—

^a Values from [13].^b For TiO₂, the values shown are those typical of geological liquids [13]. In detail, the partial molar volume of this component is a function of coordination number, as illustrated in Figure 3.^c Values from [14], applicable for B₂O₃ < 15 wt %.^d For Fe₂O₃, the values shown here are taken from [15] and correspond to liquids rich in alkalis for which the coordination number of Fe³⁺ is close to 5.^e For FeO, the values shown here are taken from [16] and correspond to liquids poor or devoid of alkalis.^f Values from [17], for a SiO₂ partial molar volume of 26.75 cm³/mol at 1400 °C.^g Value from [18].

proportion of these structural roles being a sensitive function of alkali content (Chapter 7.6). Detailed investigation of the density of boron-containing liquids indicates that distinguishing threefold and fourfold boron can lead to a better reproduction of the experimental data and that the partial molar volume of a B₂O₃ component with only trigonal B³⁺ is close to the value measured in pure liquid B₂O₃ [14]. Because the speciation of B³⁺ is not generally known in the liquid at high temperature, however, it has been concluded that a single partial molar volume for the B₂O₃ component is sufficient for practical purposes, at least for liquids containing less than ~15 wt % B₂O₃ [14].

A third situation of note is that of multivalent cations, for which each oxidation state may be expected to be associated with a different partial molar volume. The case of iron (as FeO and Fe₂O₃) is of particular importance

given the large concentrations of this element in melts of geological and metallurgical interest. When investigating these liquids, the first difficulty is thus controlling and/or measuring the relative proportions of FeO and Fe₂O₃, which depend on temperature, oxygen fugacity, and melt composition (Chapter 5.6). Of note is the fact that the temperature dependence of redox ratio may thus lead to volume changes that are not simply the effect of expansivity.

Furthermore, both Fe²⁺ and Fe³⁺ exist in several coordination states, ranging from 4 to 6 (Chapter 2.6), complicating the interpretation of available volume data. The most recent considerations of this issue have thus endeavored to study liquids containing only one valence state of iron. Data from a wide range of simple alkali-bearing and alkali-free systems indicate that the partial molar volume

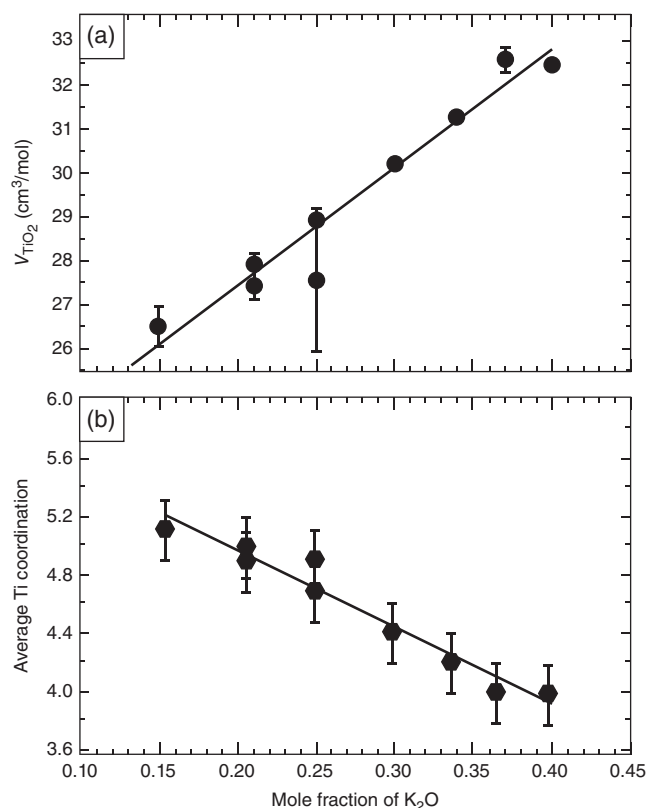


Figure 3 Effects of structural changes on the volume properties of TiO_2 -bearing potassium silicate liquids [19]. (a) Increase of the partial molar volume of the TiO_2 component with K_2O content at 1373 K. (b) Average coordination number of Ti in the quenched glasses.

of Fe_2O_3 may show significant variations, consistent with changes in average coordination state. However, the partial molar volume of Fe_2O_3 is independent of both composition and temperature in alkali-rich liquids, with a value consistent with a coordination number of Fe^{3+} of approximately five [15], which may be used for practical purposes. For FeO , measurements in a wide range of alkali-poor liquids indicate that a single temperature-dependent partial molar volume is sufficient to describe the data [16]. However, it should be appreciated that this partial molar volume is consistent with a coordination number of Fe^{2+} of almost six, leading to the possibility that for liquids in which Fe^{2+} occurs in a lower coordination state (e.g. upon addition of significant alkalis), the relevant partial molar volume could be lower.

A final case of interest is the influence of volatile species such as water or CO_2 . On the one hand, the equilibrium solubility of such species is very low at atmospheric pressure, making their influence on density minor at best at these conditions. On the other hand, at the higher pressures associated with partial melting of the Earth's

interior, these volatiles may have a significant and critical effect on liquid density. Making detailed measurements *in situ* at high temperature and pressure is particularly challenging. Alternatively, fully relaxed volatile-bearing liquids may be studied in the glass transition range at one bar using glasses quenched from high pressure. In this way the partial molar volume of H_2O has been quantified and found to be generally independent of the silicate melt composition, the total water concentration, and the speciation of water [21]. The partial molar volume of H_2O derived at 1000 °C is greater than that typical of bulk anhydrous silicates, such that the effect of 1 wt % dissolved H_2O on the density of a basaltic melt is equivalent to increasing the temperature of the melt by ~400 °C or decreasing the pressure by ~0.5 GPa.

3.2 Variations in Density over Large Temperature Ranges

In general, data from superliquidus temperatures are obtained over an interval on the order of 500 °C. In this range, a constant thermal expansivity is sufficient to describe the data, with a few rare exceptions such as molten B_2O_3 [22], the latter possibly indicating major temperature-dependent structural changes. Given that superliquidus volume generally shows ideal mixing, the same is to be expected for expansivity (that is to say, $\partial V/\partial T$, not to be confused with the thermal expansion coefficient α). This is indeed found to be the case ([6]; Table 1). For silicate melts, the strong covalent nature of the Si–O bond is such that there is little change in the Si–O length, thermal expansion being driven by expansion of the Si–O–Si angle. For this reason, the partial molar thermal expansion of SiO_2 is smaller than those of other oxides, whereas among the network-modifying oxides such as K_2O or CaO , the partial molar thermal expansion coefficients are inversely correlated with cation field strength, a trend also observed for partial molar heat capacities.

Given that relaxed liquid volumes and expansivities can also be defined just above the glass transition, combining all available data provides access to variations in volume over a temperature interval that is typically in excess of 1000 °C. If a single V – T coordinate at the fictive temperature is used, within nominal experimental error, a case might be made for expansivities that are constant over this entire temperature range. However, if all available measurements in the glass transition range are used, including multiple V – T coordinates and expansivities derived from the equivalence of volume and enthalpy relaxation, it becomes clear that expansivity typically decreases with increasing temperature (Figure 4). This decrease in expansivity appears most pronounced in depolymerized melts of low silica and alumina content,

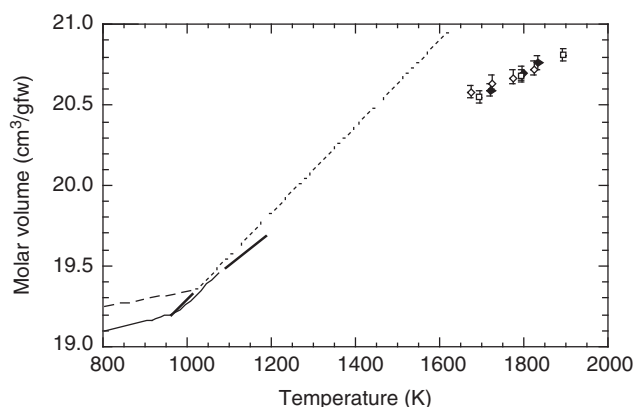


Figure 4 Temperature-dependent nature of the thermal expansion coefficient of $\text{CaMgSi}_2\text{O}_6$ liquid [1]. Thick line at ~ 1000 K: direct volume measurements [1]. Other line in the glass transition range: values derived from the assumed equivalence of structural and enthalpy relaxation [3]. Thin dashed line: extrapolation with a constant thermal expansion coefficient of the volumes measured in the glass transition range, not matching the individual measurements made at superliquidus temperature with a double-bob Archimedes technique.

such as diopside ($\text{CaMgSi}_2\text{O}_6$) melt (Figure 4), but less prominent in more polymerized liquids [1]. These data therefore argue for caution when extrapolating predictive models outside of the range where experimental data were collected.

Below the glass transition, density continues to be a function of temperature, but then expansivity values become those typical of solids, i.e. much lower than those of fully relaxed liquids. From a theoretical point of view, calculation of room-temperature density requires knowledge of the fictive temperature, the density of the liquid at that temperature, and the expansivity of the glass. In practice, glass densities can be calculated to a reasonable approximation with the partial molar values derived from extensive databases obtained on usual samples, typically obtained by the glassmaking industry (e.g. [23]).

3.3 Variations in Density with Pressure

As indicated above, the compressibility of superliquidus melts can be measured by ultrasound techniques if the density is known. Since the 1980s liquids covering a wide enough range of composition have been studied at one bar to quantify the compressibility of individual oxide components within the framework of Eq. (1) (e.g. [6, 13]). Indeed, once elements with multiple valence states and/or coordination numbers are taken account of, it is found that a set of partial molar compressibilities (expressed as $\partial V/\partial P$, not β) is sufficient to describe the pressure dependence of complex liquids (Table 1). For silicate melts, the open structure and strongly covalent

nature of the Si–O bond are such that low-pressure compression takes place through changes in the Si–O–Si angle, leading to a partial molar compressibility for SiO_2 that is high compared with those of network-modifying oxides. Among the network modifiers, there is again a negative correlation between compressibility and cation field strength. In detail, the compressibility in ternary aluminosilicate liquids appears to have non-ideal contributions, with excess terms between Al_2O_3 and both CaO and Na_2O in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems, indicating complexities and differences in compression mechanisms [24].

One can highlight such complexities by combining 1-bar data, low-pressure compressibility, sink/float data, and shock-wave data for a given composition to follow the variation of volume over a wide range of pressure. Where this is possible, volume changes are typically described by empirical equations of state (EOS) inspired by those used for crystalline materials, for example, the Birch–Murnaghan equation:

$$P = \frac{3}{2}K_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4}(K'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] + \frac{3}{8} \left[K_0 K''_0 + (K'_0 - 4)(K'_0 - 3) + \frac{35}{9} \right] \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right]^2 + \dots \right\}, \quad (4)$$

where K_0 , K'_0 , and K''_0 are the bulk modulus and its first- and second-order pressure derivatives, all for $P = 1$ bar. For molten silicates the bulk modulus increases with increasing pressure, and for a given liquid, a single equation may typically be fitted to all available volume–pressure data across the widest pressure range possible. For example, a single third-order Birch–Murnaghan isentrope centered at 1 bar and 1573 K plus a Mie–Grüneisen thermal pressure approximation reproduces the measured volumes of fayalite melt (Fe_2SiO_4) from room pressure to 161 GPa [25]. However, *in situ* quantification of the compressibility of fayalite liquid at pressures near 5 GPa is not in agreement with the value derived from the previously proposed EOS over the relevant pressure range [9].

This example illustrates that equations of state used successfully for crystalline solids may not necessarily be applicable to molten oxides over large pressure ranges. The reason for this is that, in contrast to crystalline materials, melts may experience gradual changes in the coordination number of one or more cations over certain pressure intervals. For example, in fayalite liquid, the coordination state of Fe increases from ~ 5 to ~ 7 between room pressure and 7.5 GPa, explaining the “anomalous” variation of compressibility. A similar transition, albeit

at higher pressure, has also been proposed for Mg in liquid forsterite (Mg_2SiO_4). Likewise, B, Ge, Al, and Si undergo transitions to higher coordination number over a different pressure ranges, B^{3+} and Al^{3+} at pressures lower than 5 GPa, whereas conversion of Ge and Si from fourfold through fivefold to sixfold coordination takes place at pressures of 5–10 and 20–40 GPa for pure GeO and SiO_2 respectively [9], although some interesting amorphous–amorphous transitions may also occur in these latter two systems (Chapter 3.9).

Similar transitions are also found for static compression of amorphous solids and even for crystalline materials that are observed to undergo amorphization when subjected to GPa pressures (Chapter 3.10). All of these structural changes are expected to influence bulk density. In the liquid state they should in principle be taken into account when defining and fitting a volume–pressure–temperature equation of state. On the other hand, given the unrelaxed nature of glasses, care must be taken when interpreting density variations of amorphous solids. This care involves both quantifying the fictive pressure of the glass if it is formed by cooling of a liquid at high pressure and identifying permanent vs. reversible changes in density upon compression/decompression.

4 Practical Applications

One of the most obvious practical consequences of density changes concerns the variations in volume associated with cooling through the glass transition, which is commonly used in physical tempering (Chapter 3.12). In the glassy state, volume changes are also important if the glass is in contact with a substrate, as a difference in expansivity can result in the generation of stresses at the interface during heating/cooling cycles. The same is also true for materials that contain an intimate mixture of glass and crystals, for example, glass ceramics used as kitchen hotplates. Independently of the interfaces between a glass and other materials, the thermal expansivity of amorphous oxides may be of importance in itself for certain applications, in particular those where stringent constraints on the geometry of optical path are required. The mirrors and lenses used for astronomical telescopes, including the Hubble space telescope, are a particularly good example of such an application where ultralow expansivity is required. Such glasses are typically a mixture of SiO_2 and TiO_2 , particularly refractory compositions that require innovative fabrication processes such as flame hydrolysis.

In addition to their relevance to industrial applications, the volumes of molten oxides are also of considerable importance in geological systems. Notwithstanding the question of convection alluded to in the Introduction,

the solubility and partitioning behavior of minor elements in silicate melts are directly influenced by liquid density. For example, the solubility limit of noble gases (He, Ar, etc.) in silicate melts is a function of the “ionic porosity” of the liquid, that is to say, a measure of the free volume that it not occupied by the atoms. One consequence of this fact is that dramatic decreases in solubility may occur at high pressure as the density of the liquid increases as a result of structural modifications such as changes in the coordination states of network-forming cations (e.g. [26]). Furthermore, from a thermodynamic standpoint, partial molar volumes also influence how oxide components will partition between liquid and solid phases, as illustrated for metal–silicate partitioning of the oxides GeO_2 and Ga_2O_3 [27].

Finally, as a fundamental contribution to the pressure dependence of free energy, volume has a critical influence on high-pressure phase equilibria. This is most readily illustrated by the well-known Clausius–Clapeyron relation stating that the pressure dependence of the fusion temperature of a congruently melting phase is

$$\left(\frac{dP}{dT}\right) = \left(\frac{\Delta S}{\Delta V}\right), \quad (5)$$

where ΔS and ΔV are the entropy and volume of fusion. Because the entropy of a liquid is always greater than that of a solid of the same composition, this relation implies that the sign of the slope of the liquidus is determined by the density difference between the solid and liquid. Given that the compressibility of liquids is generally greater than that of solids, volumes of fusion qualitatively decrease with increasing pressure and may even become negative (i.e. liquids are denser than crystals). In this case the Clapeyron slope may vary from positive to negative, the melting temperature being independent of pressure where crystal and liquid have the same density. In more complex multicomponent systems, the situation is not so simple, and neutral buoyancy is not necessarily related to a change in sign of the liquidus slope (e.g. [28]). On the other hand, the question of neutral buoyancy during melting of planetary mantles is a question of some significant interest given that such a “density trap” could have significant geochemical and geophysical consequences, so even today this possibility raises significant interest in the geological community [29].

5 Perspectives

Over the coming years, a better understanding the density of amorphous oxides will ultimately be driven by new experimental data that constrain the details of volume changes as a function of composition, temperature, and pressure. In this respect, direct determination of derivative

properties such as expansivity and compressibility, in particular at high pressure, will be particularly important. New and innovative techniques involving synchrotron radiation may help make significant progress (e.g. [9]), although solid–liquid partitioning behavior at high pressure remains an approach that may have more to offer (e.g. [30]). In any case, it is becoming increasingly clear that detailed interpretation of volume data cannot be made without quantification of the structure of the melt and any changes in structure that may occur upon heating and/or compression. The possibility to study liquids *in situ* at high pressures and temperatures will be of critical importance given that quenched glasses represent the structure of the liquid at a single P – T coordinate and that retrieval of the relevant fictive temperatures and pressures is not a trivial issue (e.g. [31]). Here again synchrotron-based techniques, including new approaches such as X-ray Raman scattering, may help make significant breakthroughs. Finally, the dramatic increases in computing power are revolutionizing techniques based upon numerical modeling such as molecular dynamics and *ab initio* calculations (Chapters 2.9 and 2.10). The temperature domain accessible with these techniques is now comparable to that of laboratory experiments, and the number of particles used is sufficiently large to be representative of a bulk liquids. For these reasons, such modeling efforts will undoubtedly lead to new insight concerning how volume and structure are related (e.g. [32]).

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3.6

Thermodynamic Properties of Oxide Glasses and Liquids

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1 Introduction

In Molière's famous seventeenth-century play *The Middle-Class Gentleman*, the main character Mr. Jourdain is a *nouveau riche* who is delighted to learn from his Master of philosophy that he had been speaking in *prose* for 40 years without knowing it. Would ancient glassmakers have been proud to learn that they had been likewise unknowingly practicing *thermodynamics* ever since the beginnings of their craft millennia earlier? Along with their fellow ceramists and metallurgists, they did it empirically to make the best out of their limited fuel and material resources. When the new science of thermodynamics eventually emerged at the beginning of the nineteenth century, fundamental insights were at last gained to improve the energy efficiency of high-temperature processes (Chapter 10.9). Leaving aside the glass itself, interest was first paid to the combustion reactions and heat storage by refractory materials. Since then, however, glass has entered the scene with approaches that have progressively become fairly complex as exemplified in widely different fields such as energy-efficiency assessments (Chapter 9.8), fluid-dynamics simulations of the whole melting and forming processes (Chapter 1.7), and melting reactions (Chapter 1.3) to which the present chapter is most relevant.

In glassmaking, the main thermal properties required for thermodynamic calculations are the high-temperature heat capacities (C_p) and enthalpies of formation (ΔH_f°) of the melts from the raw materials. Interestingly, such measurements were pioneered in the late nineteenth century by geophysicists at the request of

William Thomson (1824–1907), better known as Lord Kelvin, within the context of the controversy over the age of the Earth ([1] and ref. therein). Since then, interest in the thermodynamic properties of glasses and melts has been strongly enhanced by the development of phase-equilibria calculations (Chapter 5.3), which are now extensively performed to predict liquidus temperatures under most varied conditions in industry as well as in geology.

These models are only as good as their input data are. In this respect, an important practical difficulty stems from the wide composition ranges to be dealt with. This constraint makes it necessary to establish additional models for predicting reliably these input data as a function of not only composition but also temperature and, in geophysics, of pressure. Such models can be purely empirical, but it is preferable to give them a physical basis and to relate them to well-defined structural features for interpolations and, still more, for extrapolations made outside the composition ranges from which they have been established. In addition, one should not overlook the fact that the glassy state raises by itself interesting thermodynamic problems, especially at low temperatures (Chapter 3.4), which are related to the fundamental problem of the glass transition (Chapter 3.3).

In the present chapter, the operational applicability of the concept of entropy (S) to glasses in relation to their non-equilibrium nature must be justified before the experimental methods used to determine thermodynamic properties from the vicinity of 0 K to superliquidus temperatures are briefly summarized. The effects of chemical composition on thermodynamic properties can then be reviewed. Including such issues as the boson peak and residual entropy, the heat capacity and entropy are examined in four distinct temperature ranges: (i) below 50 K, where medium-range order is mainly involved; (ii) up to 300 K,

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where the influence of short-range order prevails; (iii) between room temperature and the glass transition, where compositional effects tend to vanish; (iv) above the glass transition, where much complexity is introduced by configurational degrees of freedom. Finally, the problems raised by determinations of enthalpies of mixing and of formation are briefly addressed. Because these topics are treated elsewhere, the physics of low-temperature heat capacity anomalies (Chapter 3.4) as well as thermal conductivities and diffusivities (Chapter 4.5) are not dealt with.

2 Thermodynamic Functions

2.1 The Entropy Problem

Determining the entropy change between two thermodynamic states requires the existence of a reversible pathway between them. The fact that glasses are nonequilibrium substances may thus seem to be problematic in this respect. Below the glass transition range, however, the structure of a glass is fixed so that any irreversible relaxation can be neglected during a calorimetric measurement. It is through the glass transition that difficulties arise since heat capacities measured upon heating and cooling differ, and so do entropy variations between two temperatures calculated along these distinct pathways (cf. Chapter 10.11). But the entropy created irreversibly across the glass transition is small enough to be operationally neglected and to allow the residual entropy of the glass at 0 K to be determined from calorimetric cycles involving the crystalline, liquid, and glass forms of substance [2]. The procedure has also been followed for other nonequilibrium systems such as ice, CO, and other orientationally disordered crystals with the appropriate thermochemical cycles (e.g. [3]).

Although long accepted [4], the notion of residual entropies at 0 K for amorphous or disordered substances has recently been rejected as inconsistent with the fact that the loss of ergodicity at the actual glass transition would imply the simultaneous loss of any configurational entropy because the system would become unable to explore all its configurational states [5, 6]. Against this *kinetic* picture, simple theoretical considerations [7] and detailed analyses of calorimetric measurements [8] have supported the *conventional* view. The origin of the divergence between the two pictures is the manner in which microstates are counted in statistical-mechanical models depending on whether Gibbs or Boltzmann entropy is considered [9]. The “entropy-loss” view of the kinetic picture considers only the number of states actually visited by the system at the observational time

scale. The approach of the conventional standpoint is in contrast concerned with the probability of occurrence of the relevant states, be they actually explored or not by the system. Its important point is that energy, volume, entropy, and other extensive properties remain state variables for a system that is not in internal equilibrium. Even though more than two of these variables are needed to specify the state of the system, their values remain uniquely defined [9]. Such a picture is in particular consistent with the equivalence of the kinetics of structural, enthalpy, and volume relaxation observed for silicate melts [9], with the “additivity” of extensive variables over different macroscopic parts of a system [10] and with fundamental considerations of nonequilibrium thermodynamics [11].

2.2 Gibbs Free Energy and Stability

At constant temperature and pressure, the equilibrium state of a system is determined by the minimum of its Gibbs free energy (G). From a practical standpoint, the validity of the entropy concept for glasses has thus the important consequence to make determinations of their Gibbs free energies (G) possible, as long done for phases in internal equilibrium for which available data are assessed in thermodynamic tables and databases (e.g. [12]). If the standard pressure state of 0.1 MPa (1 bar) is denoted by $^\circ$ and the subscript f refers to formation properties from elements or oxides, these data sets include $C_p^\circ(T)$, $S^\circ(T)$, $\Delta H_f^\circ(T)$, and $\Delta G_f^\circ(T)$. The Gibbs free energy of formation of a phase from its constituting elements or oxides is

$$\Delta G_f^\circ(T_0) = \Delta H_f^\circ(T_0) - T_0 \Delta S_f^\circ(T_0), \quad (1)$$

whereas the enthalpy (H) and entropy (S) are related to the heat capacity by

$$dH = C_p dT, \quad (2)$$

$$dS = \frac{C_p}{T} dT. \quad (3)$$

The Gibbs free energy can then be calculated at every temperature with

$$\Delta G_f^\circ(T) = \Delta H_f^\circ(T_0) + \int_{T_0}^T \Delta C_{pf}^\circ dT - T \left(\Delta S_f^\circ(T_0) + \int_{T_0}^T \frac{\Delta C_{pf}^\circ}{T} dT \right), \quad (4)$$

where

$$S^\circ(T_0) = S^\circ(0) + \int_0^{T_0} \frac{C_p^\circ}{T} dT. \quad (5)$$

If a reversible phase transition takes place in the system at a temperature T_t between T_0 and T , it is taken into account via its enthalpy of transition $\Delta H_t(T_t)$, viz.

$$\Delta G_f^\circ(T) = \Delta H_f^\circ(T_0) + \int_{T_0}^{T_t} \Delta C_{pf}^\circ dT + \Delta_t H(T_t) + \int_{T_t}^T \Delta C_{pf}^\circ dT - T \left(\Delta S_f^\circ(T_0) + \int_{T_0}^{T_t} \frac{\Delta C_{pf}^\circ}{T} dT + \frac{\Delta_t H(T_t)}{T_t} + \int_{T_t}^T \frac{\Delta C_{pf}^\circ}{T} dT \right) \quad (6)$$

Application of Eq. (6) to phase-equilibria calculations may be simply illustrated at high temperatures with SiO_2 glass, liquid, and polymorphs. In plots made against temperature, the intersections of the calculated $\Delta G_f^\circ(T)$ delineate the respective stability limits of quartz, cristobalite, and SiO_2 glass and liquid. These limits are clearly seen if one takes one of these phases as a reference – say, cristobalite – and plot instead the differences between its $\Delta G_f^\circ(T)$ and those of cristobalite (Figure 1). Quartz appears to be the phase stable below 1100 K and to melt metastably at 1700 K whereas cristobalite melts itself at 2000 K. In practice, however, quartz can be kept for a while above 1100 K because the kinetics of its transformation into cristobalite, which depends on many other factors than the ΔG_f° of the transition, becomes rapid only above 1400 K [13]. Because C_p differences between the solid phases are small, however, the ΔG_f° curves have very similar slopes and their intersection temperatures usually have rather large uncertainties. If known independently from phase-equilibria experiments, such temperatures

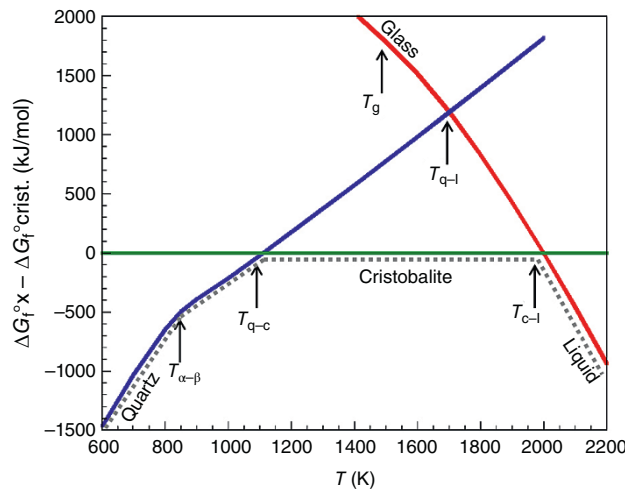


Figure 1 Stability of SiO_2 forms as indicated by the dashed line where they have the lowest Gibbs free energies of formation (Source: Data from [13]). Slope changes in the quartz and amorphous SiO_2 curves due to the α - β and glass transitions, respectively.

in turn represent important information to ensure the internal consistency of thermodynamic data sets through appropriate adjustments of the calorimetric results to within their error margins.

2.3 Experimental Approaches

2.3.1 General Remarks

The apparent complexity of Eqs. (4) and (6) should not conceal a basic simplicity since all thermodynamic properties of a substance are determined if one knows only its heat capacity as a function of temperature along with ΔH_f° at a single temperature and the entropy at 0 K, which is by convention taken to be zero for perfect crystals. At room pressure, calorimetric experiments are thus of two kinds (Table 1) depending on whether one measures enthalpy differences between two temperatures for the same phase or between different phases at the same temperature. In the former case, one measures enthalpy differences (ΔH) for a given temperature interval $\Delta T = T - T_0$. In the latter case, one is faced with the general problem raised by the sluggishness of the reactions of interest, which makes direct heat measurements impossible. One must then devise alternate routes leading from the initial to the final state considered, along which enthalpies can be measured.

2.3.2 Heat Capacity and Enthalpy

If ΔT is large in the calorimetry experiment, then one determines C_p by differentiating analytical expressions fitted to the $H(T) - H(T_0)$ measured as a function of T [13]. A major advantage of this *drop-calorimetry* method is that heat exchange does not need to be controlled at high temperatures where radiative transfer is predominant. Only the high temperature of the sample has to be measured precisely along with the heat released upon cooling at T_0 , which can be done very accurately if T_0 is close to room temperature. With transposed drop calorimetry, the sample is in contrast dropped from room temperature in a calorimeter kept at temperatures of up to 1000 K where the enthalpy absorbed is measured; the precision is not as high as in usual drop calorimetry, but the advantage is in some cases to ensure a final reproducible state for the sample.

If the ΔT and ΔH of the calorimetry experiment are in contrast small, as is the case of the heat brought to the sample in adiabatic calorimetry [14], then one assumes that $C_p = \Delta H/\Delta T$ with appropriate *curvature* corrections to account for the actual temperature dependence of the heat capacity of the sample between T_0 and T . Inaccuracies as low as of 0.1% can be achieved with adiabatic calorimetry but heat exchange between the sample and its

Table 1 Experimental calorimetric methods.

Method and property measured	Sample size	Inaccuracies	Effective measurement	Example of companies
Drop calorimetry with ice or other kinds of calorimeters $H_T - H_{T_0}$	1–10 g	400–1900 K 0.2% On derived C_p : 0.5%	Sample dropped from high (T) to low (T_0) temperature; $H_T - H_{T_0}$ proportional to the amount of ice melting as determined from the volume decrease of the transition (constant temperature at 273 K).	Self-made
Adiabatic calorimetry C_p	1–10 g	4–15 K: 5% 15–25 K: 1% 25–50 K: 0.5% 50–350 K: 0.1%	Measurement of the increase of temperature ΔT after a known input heat Q .	Self-made
Relaxation calorimetry (isoperibol) C_p	1–500 mg	0.1–300 K: around 1 and 2%	Relaxation time to reach the final temperature after an increase of temperature can be related to the global heat capacity of the sample and sample holder after calibration.	PPMS by quantum design
Differential scanning calorimetry (isoperibol) C_p	0.1–3 g	90–1500 K: 1–3%	Sample and reference heated under the same conditions at the same rate between temperatures T_1 and T_2 . Difference between the heat fluxes measured by power compensation or with a thermopile, integrated from T_1 to T_2 and divided by $T_2 - T_1$ to derive C_p . Calibration needed from known standards. Nonequilibrium measurement.	Netzsch, PerkinElmer, Setaram, etc.
Calvet-type calorimetry (isothermal) C_p	10–500 mg	300–1000 K ΔH : 1%	Heat flow caused by the phase change integrated as measured with a calibrated thermopile made up of a 3-D network of thermocouples; sample usually dropped into the calorimeter from room temperature.	Self-made, Setaram

surroundings becomes increasingly difficult to control when temperature increases, and blackbody radiation becomes significant, so that the measurements are usually restricted to temperatures lower than 400 K. This restriction also applies to the newer but slightly less accurate physical property measurement system (PPMS) with the heat capacity option [15] whose major advantage is to require samples of a few tens of mg, which are hundred times smaller than those needed for adiabatic calorimetry.

The other technique of differential scanning calorimetry (DSC) has become extensively used because it is rapid, commercially available, requires small samples of a few tens of mg, and lends itself to dynamic measurements made at heating rates of up to a few hundreds of degrees per minute. This is a modern form of differential thermal analysis in that it relies on comparisons made with a standard, generally corundum, whose heat capacity is accurately known, which is heated under conditions as similar as possible as those of the sample. Measurements with inaccuracies of 1% can be made if the heat fluxes to both sample and standard are measured with Calvet-type calibrated thermopiles made up of hundreds of thermocouples in series. The precision is less good, but the sensitivity may be higher, when only the differences in the power delivered to the sample and standard are measured with less expensive equipment. But the main limitation of

the technique is its upper temperature limit of about 1000 K for precise enough results, which severely restricts its uses for glass-forming liquids to compositions with low T_g 's. Interesting observations can nonetheless be made with some setups working up to 1650 K, but with errors of about 3% that are inappropriate for C_p measurements.

2.3.3 Enthalpies of Transformation

To determine enthalpy differences between different phases that do not react rapidly, the trick consists in measuring the enthalpy of solution into the same solvent of all the phases of interest (e.g. a glass and a crystal of the same composition). Conditions approaching those of infinite dilution are maintained so that the enthalpy of the transformation is simply given by the sum of the enthalpies of solution weighted by the stoichiometric coefficients of the reaction. With Calvet-type calorimeters, these solution-calorimetry measurements are also performed with thermopiles. They are made either close to room temperature with hydrofluoric acid, HF, which work well for alkali- and SiO_2 -rich materials [14], or near 1000 K with molten lead borates for more refractory samples that would leave undissolved fluoride residues in HF solutions [16]. If the heat capacities of the phases considered are known, the measured enthalpies of transition can then be referred to any other temperature.

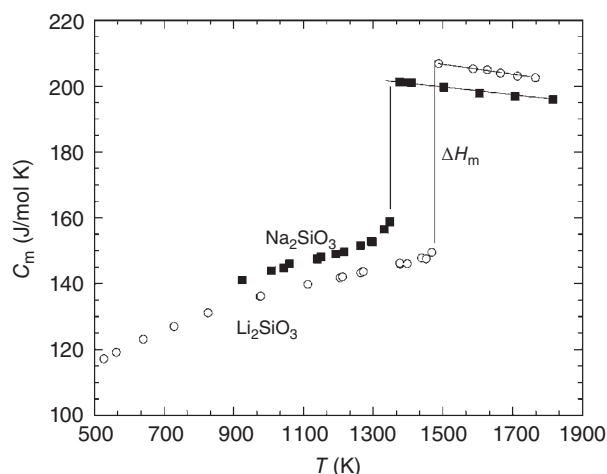


Figure 2 Enthalpies of fusion of Na_2SiO_3 and Li_2SiO_3 directly measured by drop calorimetry as discontinuities in the $C_m = (H_T - H_{273})/(T - 273)$ curves at the melting temperatures of 1362 and 1474 K, respectively (Data from [17]). Premelting effects apparent in anomalous enthalpy increases beginning 150 and 10 K below the congruent melting points of Na_2SiO_3 and Li_2SiO_3 , respectively.

The complementary nature of the two general calorimetric methods is obvious in determinations of enthalpies of fusion. Contrary to most metals and salts, which crystallize readily upon melt cooling, oxide compounds generally vitrify at least partially. Direct measurements of the enthalpy of crystallization are thus restricted to very few cases where no glass at all is present in the sample after rapid cooling in the calorimeter (Figure 2). A more complicated procedure must in general be followed. It consists in combining the enthalpy of *vitrification* of the crystal measured by solution calorimetry at a convenient temperature T_v with the relevant enthalpy or C_p data to derive the enthalpy of fusion at the higher melting temperature T_m (Figure 3). This procedure has thus been followed to determine most of the data available for about 30 oxides and silicates [18, 19]. Because it increases with the interval $T_m - T_v$ and the C_p difference between the liquid and crystal phases, the enthalpy of fusion can actually be twice as great as the enthalpy of vitrification so that the latter generally does not represent a good approximation for the former.

2.4 The Influence of Thermal History

In view of the C_p decrease observed upon cooling at the glass transition, glasses quenched at different rates have necessarily different enthalpies (Figure 3). The enthalpy difference between two glasses having fictive temperatures T_{f2} and T_{f1} is then given by

$$\begin{aligned} \Delta H_{v2} - \Delta H_{v1} &= (C_{pl}(T_g) - C_{pg}(T_g))(T_{f2} - T_{f1}) \\ &= \Delta C_p(T_g)(T_{f2} - T_{f1}), \end{aligned} \quad (7)$$

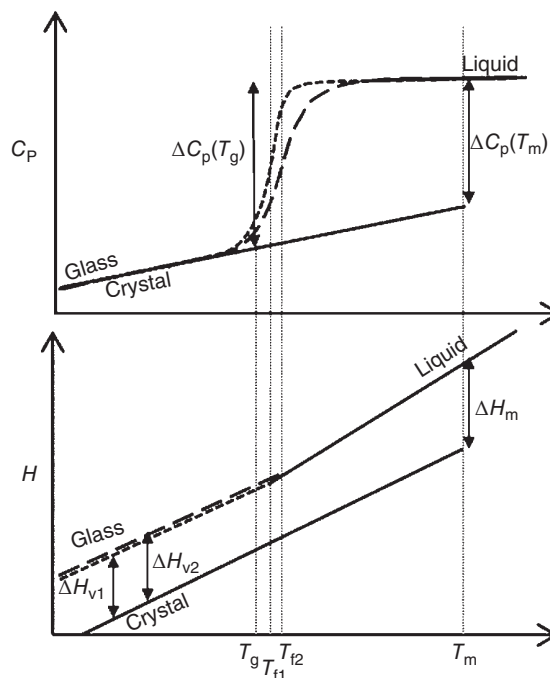


Figure 3 Heat capacity and enthalpy above room temperature of the crystal, glass, and liquid phases of a substance melting congruently at T_m . Enthalpy of fusion at T_m determined from the enthalpy of vitrification measured by solution calorimetry at T_v and the heat capacities of the amorphous and crystalline phases between T_v and T_m . Glass enthalpy and C_p decreases at the glass transition represented for slowly and rapidly cooled glasses of fictive temperatures T_{f1} and T_{f2} , respectively.

where the subscripts l and g refer to the supercooled liquid and glass, respectively (Figure 3).

Except for hyperquenched glasses (Chapter 3.8), these effects can often be neglected because very large differences in quenching rates are needed to produce variations of fictive temperatures greater than a few tens of degrees [20]. An additional simplifying feature is that the influence of the fictive temperature on the heat capacity of the glass can be neglected as long as temperatures are not lower than about 50 K [20]. There is, however, another instance where fictive-temperature effects must be considered. It is the determination of enthalpies of mixing between *melts* from solution-calorimetry measurements made on *glasses* with widely different fictive temperatures. Because enthalpies of mixing are typically 10 times smaller than enthalpies of fusion, corrections made with Eq. (7) are no longer negligible. Meaningful results are thus obtained only if the measurements are referred with this equation either to the same fictive temperature or to a common equilibrium temperature [21] as clearly illustrated by the enthalpies of mixing in the $\text{Na}_2\text{O}-\text{SiO}_2$ system for which differences in fictive temperatures between SiO_2 and the Na-bearing glasses investigated could reach 800 K [22].

3 Low-temperature Heat Capacity and Entropy

3.1 From the Vibrational Density of States to the Heat Capacity

Like that of any solids, the heat capacity of glasses is a measure of the progressive excitation of atomic vibrations when thermal energy is brought to the substance and increases its temperature. In this respect, the fundamental feature is the vibrational density of states $g(\nu)$, i.e. the distribution of the number of vibrational modes as a function of frequency (Figure 4). For each vibration mode of frequency ν , the heat capacity is given by an Einstein function

$$c_\nu(T) = \frac{x^2 e^x}{(e^x - 1)^2}, \quad (8)$$

where x stands for $h\nu/kT$, and h and k for Planck and Boltzmann constants. The heat capacity of the glass is the integral of Eq. (7) over $g(\nu)$ from 0 to the maximum vibrational frequency ν_m :

$$C_V(T) = \int_0^{\nu_m} c_\nu(T) g(\nu) d\nu. \quad (9)$$

Neglecting the very small differences existing below 300 K between the isobaric (C_p) and isochoric (C_V) heat capacities, one then calculates the vibrational entropy from

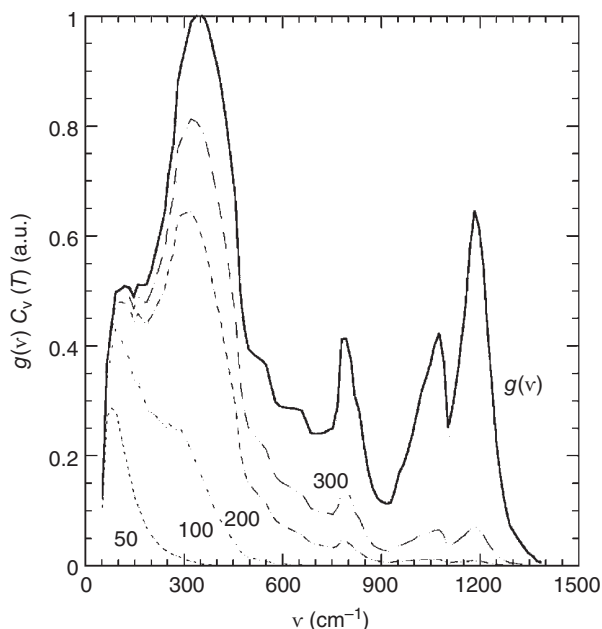


Figure 4 Relationship between the vibrational density of states, $g(\nu)$, of SiO_2 glass and the heat capacity as given by the areas below the $g(\nu)c_\nu(T)$ functions plotted at the indicated temperatures. Data from [23].

$$S_{298} - S_0 = \int_0^{298} \frac{C_p}{T} dT, \quad (10)$$

where the residual entropy S_0 cannot be omitted because it is not zero for glasses and other disordered substances.

With increasing temperatures, modes of progressively increasing frequency (and energy) contribute to the heat capacity. For SiO_2 glass, only modes of frequencies lower than 200, 400, and 600 cm^{-1} contribute significantly to C_p below about 50, 100, and 200 K, respectively (Figure 4). Of course, these regimes do not have sharp boundaries but such simple considerations are useful to discuss the composition dependence of low-temperature heat capacities and entropies for which there is now a wealth of experimental data. These low-frequency modes involve either weak bonds or the motion of a large number of atoms and, as such, can be considered as probes of medium-range order. Indeed, it is only in this temperature range that a dependence of C_p on the thermal history of the glass is detected, the heat capacity being higher for samples with higher fictive temperatures and lower density (e.g. [20]). But C_p values below 50 K are so small that they barely contribute to the room-temperature entropy as given by Eq. (10). High-frequency modes in contrast are a direct reflection of short-range order, which involves the strongest atomic interactions and dominate the room-temperature entropy.

3.2 Oxygen Coordination of Network-modifying Cations

In a first approximation, atomic vibrations in solids may be considered to be harmonic oscillations whose frequencies decrease as the mass of the atoms involved increases and increase with the strength of their bonding (cf. $\nu = 1/[2\pi(\mu/k)^{1/2}]$ of the diatomic molecule, where μ is the reduced mass and k the force constant). For disilicate glasses (Figure 5), the heat capacities thus decrease from K to Na and Li as a result of increasing cation mass and of the increase in average bond strength caused by the decrease of the ionic radius of the alkali. In addition, they are higher for glasses than for their isochemical crystals as a result of a larger volume, which affects acoustic modes through a decrease of the bulk modulus, and of a bond-strength disordering in the network at constant volume [25]. A third factor is the presence at low frequency of the excess of vibrational modes to be described below in Section 3.5.

Nevertheless, the overall similarity of the data for glasses and crystals excludes markedly different short-range order not only in disilicate glasses and crystals but also, more generally, in binary $\text{SiO}_2\text{-M}_2\text{O}$ systems for which vibrational entropies vary linearly up to the metasilicate compositions (Figure 6). Hence, especially for potassium silicates, the average oxygen coordination

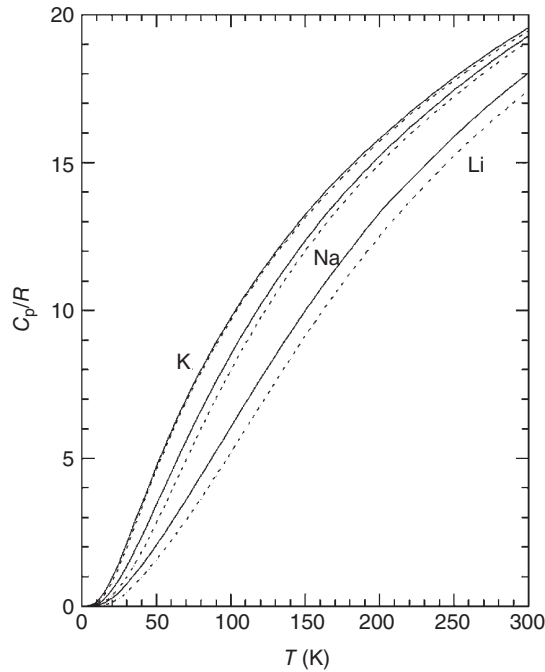


Figure 5 Low-temperature heat capacities of alkali disilicate $M_2Si_2O_5$ glasses (solid curves) and crystals (dashed curves). Data from [24].

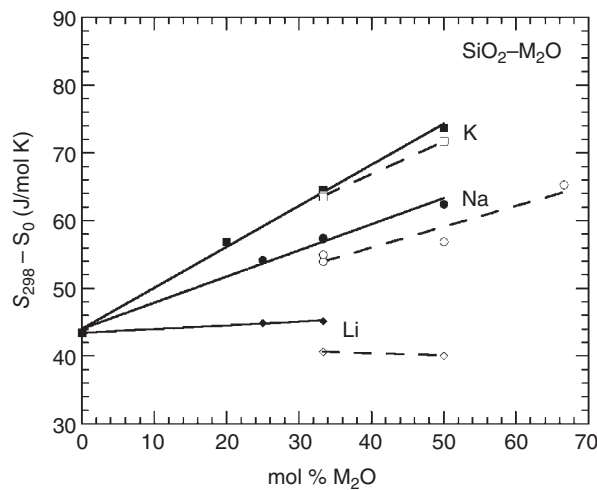


Figure 6 Vibrational entropy of alkali silicate glasses (solid symbols) and crystals (open symbols). Source: Data from [33] and de Ligny (unpublished results).

number should be close to the value of about 5 that holds in crystals.

3.3 Oxygen Coordination of Network-Forming Cations

That the effects of oxygen coordination, or atomic packing, are much more important than those of volume (at constant coordination) is clearly illustrated by the

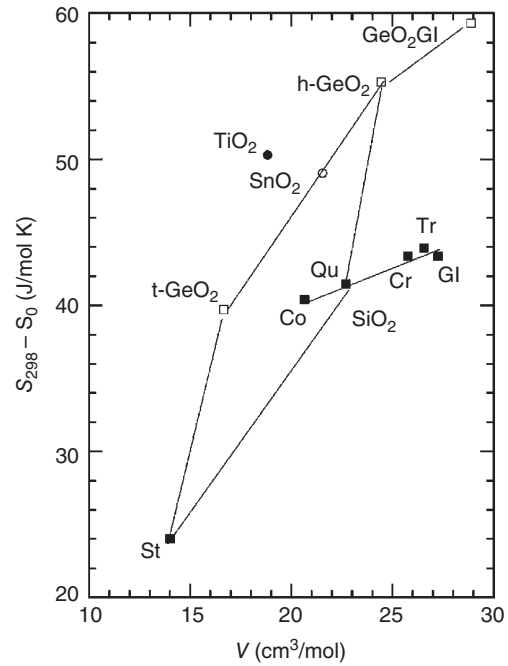


Figure 7 Vibrational entropy of SiO_2 and GeO_2 glasses and polymorphs against the molar volume of the phases. SiO_2 : Gl (glass), Qu (quartz), Cr (cristobalite), Tr (tridymite), St (stishovite), and Co (coesite). GeO_2 : Gl (glass), t- (tetragonal form), and h- (hexagonal form). Data for SnO_2 (cassiterite) and TiO_2 (rutile) added to complement the trend for tetragonal crystals. Data from [26, 27].

network-forming cations Si^{4+} and Ge^{4+} . For the isostructural forms of SiO_2 and GeO_2 (Figure 7), the vibrational entropy is much higher for tetrahedral than for octahedral coordination. Because Si—O and Ge—O bond distances are shorter for the former coordination than for the latter, the internal vibrational modes have lower frequencies in SiO_4 and GeO_4 tetrahedra than in SiO_6 and GeO_6 octahedra, but the ensuing lower contributions to the heat capacities are more than compensated by the effects of the C_p decreases of the lattice modes that are due to the shorter Si—Si and Ge—Ge distances between second-nearest neighbors in the dense, high-pressure phases.

A similar effect of the change of four- to sixfold coordination of aluminum is apparent in the $S_{298} - S_0$ data of sodium and calcium aluminosilicates (Figure 8). In both series, the vibrational entropies vary linearly from pure SiO_2 to the meta-aluminous compositions for glasses and low-pressure crystals, in accordance with the tetrahedral coordination reported for both Si^{4+} and Al^{3+} [19]. In contrast, the high-pressure phases of crystalline jadeite (Jd, $NaAlSi_2O_6$) and Ca-Tschermak pyroxene (CaTs, $CaAl_2SiO_6$) have entropies departing negatively from these trends because all or some of their Al is sixfold coordinated.

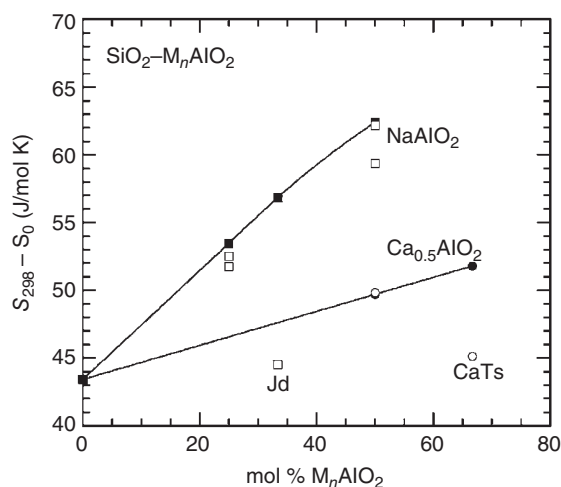


Figure 8 Vibrational entropy of crystals (open squares) and glasses (solid circles) along the joins $\text{SiO}_2\text{--NaAlO}_2$ and $\text{SiO}_2\text{--Ca}_{0.5}\text{AlO}_2$. Minerals with six-coordinated Al: Jd ($\text{NaAlSi}_2\text{O}_6$) and Ca-Ts ($\text{CaAl}_2\text{SiO}_6$). Data from [26].

3.4 Partial Molar Entropy of Oxides in Silicate Glasses

The determining influence of short-range order on vibrational properties is also demonstrated by the fact that the entropy of silicate crystals may be calculated as a sum of entropy coefficients pertaining to oxide components characterized by the coordination number of the cation [28]. In view of the continuous nature of glass solutions, the same procedure can be applied to derive partial molar heat capacities and vibrational entropies for oxides in glasses (Table 2). The generally additive nature of $S_{298} - S_0$ (Figures 6 and 8) is confirmed by the fact that data available for about 50 different compositions can be reproduced to better than 1% with a set of composition-independent partial molar entropies.

As expected, the influence of Al speciation in aluminosilicates is clear since partial molar heat capacities (Figure 9) and entropies decrease from four- to five- and then sixfold coordination [30]. Another noteworthy feature is that two different Na_2O and K_2O components must be distinguished depending on whether the alkali element is “free” or is associated as a charge compensator with tetrahedral Al [26]. The higher entropies calculated in the latter cases indicate that association with Al causes the coordination number of the alkali to increase from the aforementioned number of about 5 to a much higher value similar to those determined for tectosilicates. But a single entropy is derived for Ca and for Mg when transforming from network modifier to a charge compensator, indicating that in contrast the environment of alkali earth

Table 2 Partial molar relative entropies of oxides in silicate glasses, and entropy coefficients of oxides in crystals for the coordination numbers indicated by Roman numbers.

Oxide	Glasses	Crystals
SiO_2	43.37	40.3 (IV)–24.0 (VI) ^a
GeO_2	59.33	55.3 (IV)–39.7 (VI)
$^{\text{IV}}\text{Al}_2\text{O}_3$ ^b	72.8	72.1–43.8 ^c
$^{\text{V}}\text{Al}_2\text{O}_3$	48.5	59
$^{\text{VI}}\text{Al}_2\text{O}_3$	45	42
$^{\text{III}}\text{B}_2\text{O}_3$ ^c	63.7	
$^{\text{III}}\text{B}_2\text{O}_3$ ^c	70.2	54
$^{\text{IV}}\text{B}_2\text{O}_3$	33.5	
MgO	30.7	26.7 (VI)–27.7 (VII)
CaO	42.8	39.6 (VI)–38.7 (VIII)
Li_2O	49.0	38.5 (IV–V)
Na_2O	85 ^d	76 (IV–V)
	96.7 ^a	97.3 (IX)
K_2O	108 ^d	101 (V–VI)
	119.1 ^a	114.3–120.4
FeO	56.1	43.2 (IV–VIII)
Fe_2O_3	116	85 (VIII)

^a For Al charge-compensating alkali.

^b Average value of 69.1 to be used if Al speciation is unknown.

^c Three-coordinate boron belonging either to boroxol rings ($^{\text{III}}\text{B}_2\text{O}_3$) or “free” ($^{\text{III}}\text{B}_2\text{O}_3$) [Richet, unpublished]. Average value of 37.36 J/mol K for pure B_2O_3 glass.

^d In Al-free silicates.

Source: Data (J/mol K) from [23, 26, 29–31] for glasses and [28] for crystals.

cations does not change much upon a less strong association with two tetrahedral Al^{3+} ions. As for boron, one must not only assign widely different values to three- and fourfold coordination but distinguish in the former between borons that belong to the so-called boroxol rings (Chapter 7.6) and the others (Table 2).

3.5 Calorimetric Boson Peak

For some glasses [23], additivity of the heat capacity can break down below about 50 K where there exist strong positive deviations with respect to the Debye T^3 laws commonly observed near 0 K by crystals. This calorimetric anomaly originates in an excess of modes found between 30 and 150 cm^{-1} in the vibrational density of states, known as the boson peak (Chapter 3.4), with respect to Debye model that considers a solid as an

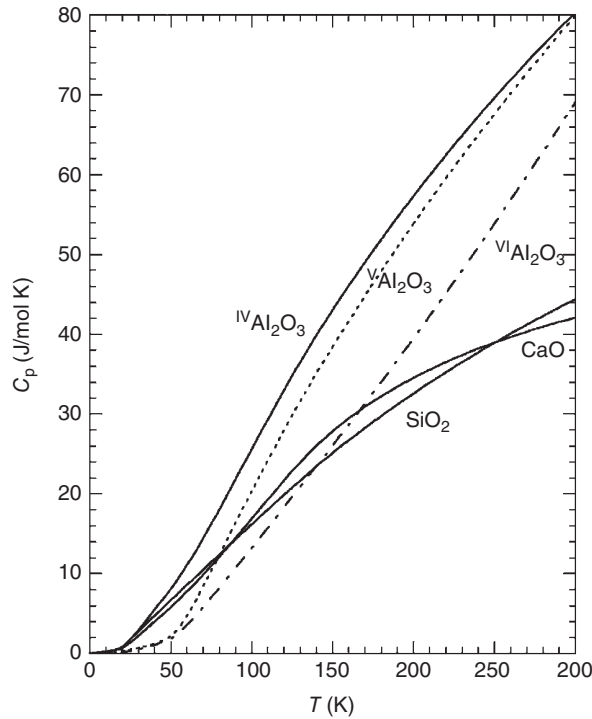


Figure 9 Influence of the coordination state of aluminum on the partial molar heat capacities of Al_2O_3 in aluminosilicate glasses, compared with those of CaO and SiO_2 . [30].

isotropic continuum in which longitudinal and transversal acoustic waves propagate with constant velocities. Owing to this common reference to Debye model, the calorimetric anomaly will also be referred to as a boson peak. It is in fact not peculiar to glasses and other disordered solids (Chapter 3.4). As indicated by peaks in plots of C_p/T^3 against T , the calorimetric anomaly is even greater for cristobalite than for SiO_2 glass although it markedly decreases to quartz and coesite and vanishes for stishovite, which does follow Debye law (Figure 10). For SiO_2 glass, the boson peak is assigned to coupled librations of the corner-shared SiO_4 tetrahedra (at 0.3–4 THz frequencies) coexisting with sound waves [32]. Its marked decrease can also be assigned first to an increasingly compact arrangement of SiO_4 tetrahedra, which hinders librational motion, and then to the change from four- to sixfold Si coordination, which makes it impossible [19].

In binary alkali silicate glasses, the calorimetric boson peak increases in intensity and decreases in temperature from Li to Na and K (Figure 11) as replacement of large and heavy K^+ ions by smaller, more tightly bonded Li^+ ions shifts vibrational modes to lower frequencies. Additional insights can be gained in this respect from the inversions of Eq. (8) made to derive the low-frequency

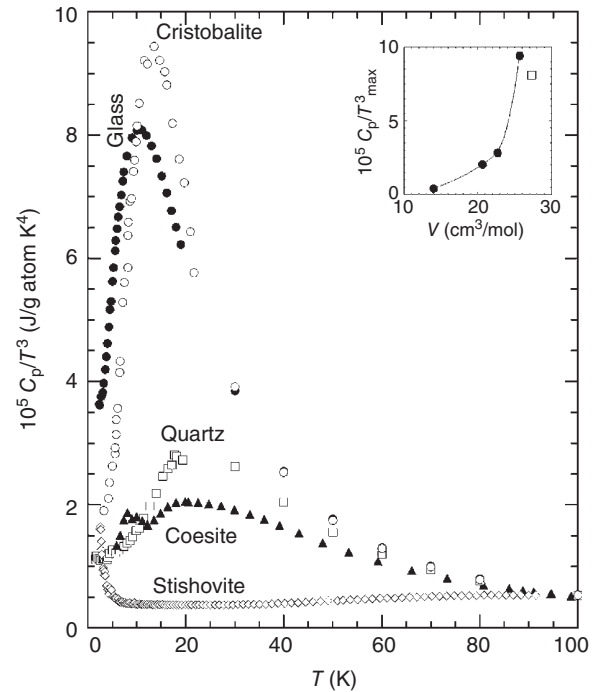


Figure 10 Calorimetric boson peak of SiO_2 glass and polymorphs. Data sources in [19, 27]. Inset: maximum of the boson peak against the molar volume of the polymorphs (open square: SiO_2 glass).

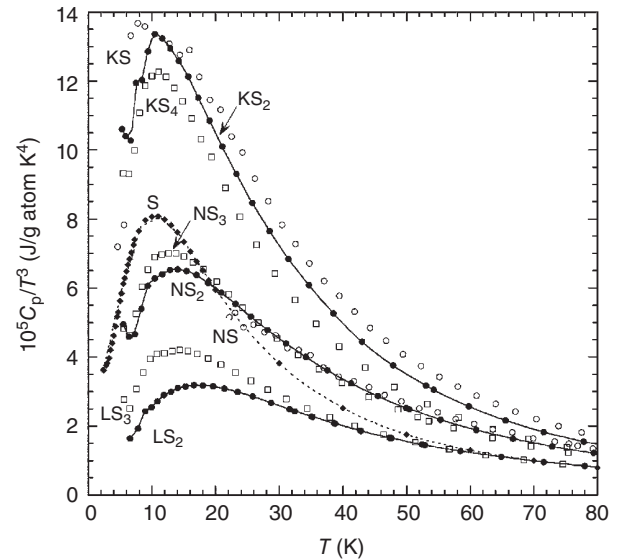


Figure 11 Calorimetric boson peak of SiO_2 (S) and alkali silicate glasses. Data from [33].

part of the vibrational density of states from C_p data. Well-defined first peaks representing the excess modes are obtained in this way [33]. As expected from the linear trends of the input C_p data, their positions and intensities

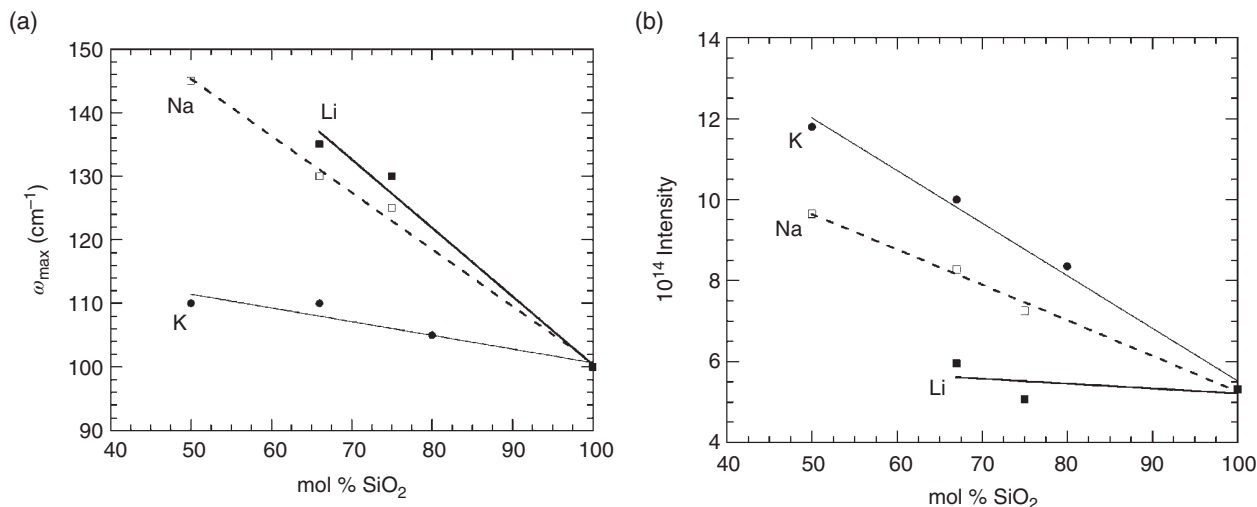


Figure 12 First peak of the vibrational density of states of alkali silicate glasses as determined by inversion of low-temperature heat capacities [33]. (a) Position of the peak. (b) Intensity.

also vary linearly with M_2O content in alkali silicates (Figure 12) and point to a combination of librational modes from the SiO_2 component and localized vibrational modes for network-modifying cations [33, 34]. The intensity decrease caused by network depolymerization, which restricts librational motion, is more than compensated by increasing the intensity of localized vibrations. Despite the wide variations found in the position and magnitude of the boson peak, another strikingly simple feature is the collapse of all data on a single master curve when the temperature and maximum of the peaks are used as normalizing parameters for plotting the experimental data (Figure 13). But this universal representation remains to be accounted theoretically.

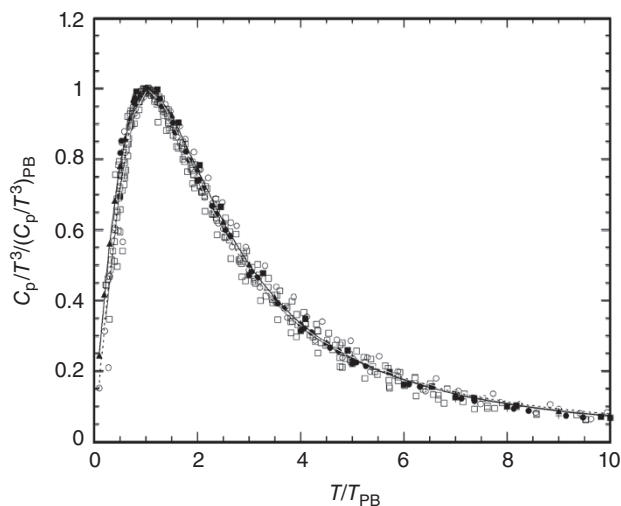


Figure 13 Universal representation of the calorimetric boson peak with the reduced variables $T/T_{\max}$ and $C_p/C_{p\max}$. Data for 20 silicate, aluminosilicate, and oxynitride glasses from [33, 34] and ref. therein.

4 High-temperature Properties

4.1 Glasses

Above room temperature (Figure 14), an important feature is that the glass transition takes place when the heat capacity becomes close to the Dulong and Petit harmonic limit of $3R/g$ atom where R is the gas constant [35]. It follows that any composition dependence tends to vanish at the glass transition where only the number of atoms in the formula unit eventually matters. Hence, the C_p

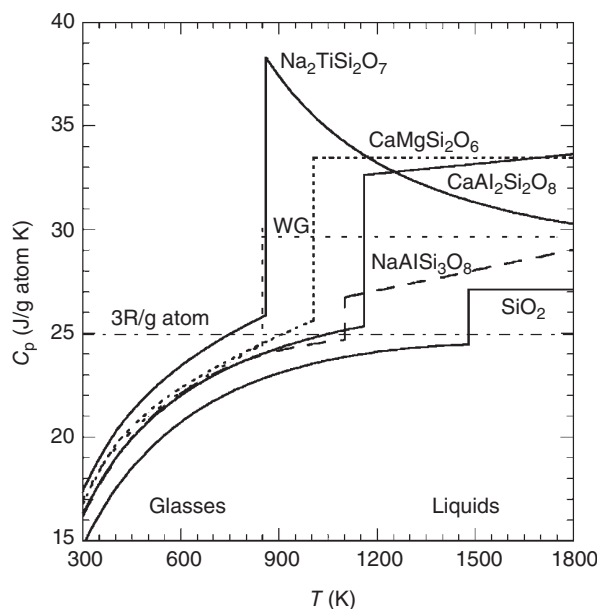


Figure 14 The highly contrasting changes in the heat capacities of some silicate at the glass transition. WG: window glass. Data sources in [19].

Table 3 Partial molar heat capacities of oxides in glasses, $C_{pi} = a_i + b_iT + c_i/T^2 + d_i/T^{1/2}$ (J/mol K).

Oxide	a_i	$10^3 b_i$	$10^{-5} c_i$	d_i
SiO ₂	127.200	-10.777	4.3127	-1463.9
Na ₂ O	70.884	26.110	-3.5820	
K ₂ O	84.323	0.731	-8.2980	
CaO	39.159	18.650	-1.5230	
MgO	46.704	11.220	-13.280	
Al ₂ O ₃	175.491	-5.839	-13.470	-1370
TiO ₂	64.111	22.590	-23.020	
FeO	31.770	38.515	-0.012	
Fe ₂ O ₃	135.250	12.311	-39.098	
B ₂ O ₃	215.151	-3.435	15.836	-2920
H ₂ O	82.804		-48.274	

Source: Data from [36] and from [37] for H₂O.

additivity observed below 300 K also obtains at higher temperatures with the simplifying feature that the specification of Al and alkalis no longer needs to be considered. This feature is illustrated by the convergence of the partial molar heat capacities of the Al₂O₃ species already under way below 300 K (Figure 9), but does not hold for boron for which there remains a large C_p difference between ^{III}B₂O₃ and ^{IV}B₂O₃.

To within their error margins, available heat-capacity and relative-enthalpy data can thus be reproduced from room temperature up to the glass transition with composition-independent partial molar heat capacities of the form (Table 3),

$$C_p = \sum x_i \left(a_i + b_i T + c_i/T^2 + d_i/T^{1/2} \right), \quad (11)$$

where x_i is the mol fraction of oxide i and the coefficients for SiO₂ and B₂O₃ are simply those of the C_p expression of the pure oxide glass [36]. If additional oxides need to be considered at not too high contents, then use can be made of the heat capacities of their crystalline forms in view of the generally small differences observed between glasses and crystals.

4.2 Liquids

As long as crystallization does not take place, there is not any change in the physical properties of melts when the liquidus is crossed. This feature applies in particular to the heat capacity, which varies smoothly from the supercooled to the stable liquid domain. In practice, experimental difficulties generally stem from incipient crystallization above the glass transition and very high liquidus temperatures. In other words, only short temperature intervals can very often be investigated in either

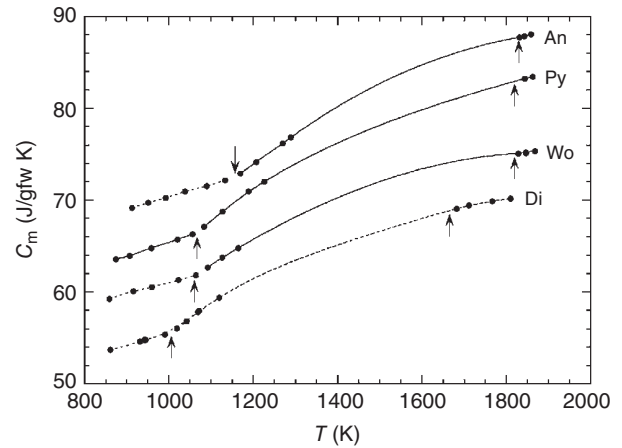


Figure 15 Mean heat capacity, $C_m = (H_T - H_{273})/(T - 273)$, of some aluminosilicate glasses and melts on both sides of the glass transition: An (CaAl₂Si₂O₈), Py (Mg₃Al₂Si₃O₁₂), Wo (CaSiO₃), and Di (CaMgSi₂O₆). Liquidus and glass transition temperatures indicated by arrows; data referred to 1 mol of oxide components; for clarity reasons, data for Py and Wo displaced upward by 3 and 5 J/gfw K, respectively. Data from [21].

domain. Not to introduce any bias, the most reliable measurements must rely on a single technique working from T_g to superliquidus temperatures. Even though quite a few valuable DSC measurements are now available, they are limited to restricted temperature intervals for low- T_g compositions for which high-temperature extrapolations are not warranted.

In the following, only drop-calorimetry results obtained up to 1850 K will thus be mentioned (Figure 15). If precise measurements are made both near T_g and at superliquidus temperatures, the *crystallization curtain* is not a great impediment, thanks to the reliable interpolations that can be made and make it, for instance, possible to ascertain whether or not the heat capacity of the liquid varies with temperature. In addition, the results yield the C_p changes at the glass transition (ΔC_p), which vary from about 10 to 50% and display extremely strong dependences on composition (Figure 14). This variety is exemplified by (i) window glass and sodium silicate melts whose heat capacities are constant over the whole temperature intervals investigated, which can reach 1000 K; (ii) titanosilicate melts, which show record high ΔC_p 's reaching 50%, followed by markedly negative values of dC_p/dT ; (iii) aluminosilicate melts, with ΔC_p values ranging from 10 to 30% and positive dC_p/dT values increasing in the order Mg, Ca, and Na in ternary systems [19]; (iv) other complexities found in borosilicates for which dC_p/dT is also variable without being correlated with B₂O₃ content [38].

It is beyond the scope of this chapter to discuss such differences. But it is worth noticing that some are reminiscent of those observed at low temperatures, which

Table 4 Partial molar heat capacities of oxides in melts, $C_{pi} = a_i + b_i T + c_i/T^2$ (J/mol K) [39].

Oxide	a_i	$10^3 b_i$	$10^{-5} c_i$
SiO ₂	81.37		
Li ₂ O	107.7		
Na ₂ O	100.6		
K ₂ O ^a	50.13	15.78	
Rb ₂ O	97.36		
BeO	46.65		
CaO	86.05		
SrO	86.12		
BaO	79.96		
ZnO	92.57		
MnO	82.73		
MgO	85.78		
PbO	55.98		
Al ₂ O ₃	27.21	94.28	
TiO ₂	75.21		875.3
FeO	78.94		
Fe ₂ O ₃	199.7		
Y ₂ O ₃	233.7		
Sb ₂ O ₃	204.8		
Bi ₂ O ₃	257.7		
La ₂ O ₃	241.8		

^a Excess $C_p = 151.7 x_{\text{SiO}_2} x_{\text{K}_2\text{O}}$ (J/mol K) to be included [39].

are assigned to the dual structural role of cations that are either network modifiers or charge compensators for tetrahedrally coordinated cations. Likewise, it is tempting to assign the unusual heat capacities of titanosilicate melts to a decreasing extent of (Ti, Si) mixing on tetrahedral sites with decreasing temperatures, which would result in the coexistence of silicate and titanate species without unmixing at the lower temperatures [19].

From a practical standpoint, the occurrence of the glass transition when the Dulong-and-Petit limit is approached makes it possible to approximate the configurational heat capacity by the simple relation [18]

$$C_p^{\text{conf}}(T) = C_{\text{pl}}(T) - C_{\text{pg}}(T_g) = C_{\text{pl}}(T) - 3nR, \quad (12)$$

where n is the number of atoms in the unit formula, which provides values as accurate as those one would determine experimentally. Although C_p additivity is clearly observed in simple systems such as Li₂O– and Na₂O–SiO₂ or MgO–Al₂O₃–SiO₂, it breaks down in Ca and Na

aluminosilicates [19]. A model with “average” partial molar heat capacities is nonetheless useful especially for chemically complex compositions for which errors usually made with simple models compensate to a large extent (Table 4).

4.3 Residual Entropies

The residual entropy of a glass, S_0 , represents the entropy frozen in at the glass transition. It increases with increasing cooling rates. It can be determined by calorimetric methods from the entropy of melting of the crystal and the appropriate integrations of heat capacities measured between 0 K and T_m for the crystal, liquid, and glass phases (Figure 16), namely

$$S_g^{\circ}(0) = S_c^{\circ}(0) + \int_0^{T_m} \frac{C_{pc}^{\circ}}{T} dT + \frac{\Delta H_m^{\circ}}{T_m} + \int_{T_m}^{T_g} \frac{C_{pl}^{\circ}}{T} dT + \int_{T_g}^0 \frac{C_{pg}^{\circ}}{T} dT. \quad (13)$$

When melting temperatures are not too high (i.e. 1900 K at most), these measurements are possible if there exists an isochemical crystal that (i) melts congruently, so as to have $\Delta S_m = \Delta H_m/T_m$ and (ii) can be considered perfect at 0 K, so as to have a zero entropy at 0 K. These practical and thermodynamic constraints are the reason

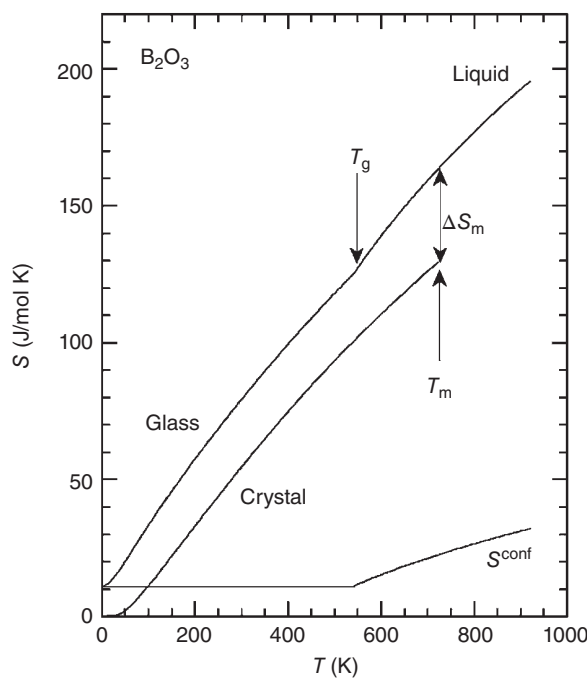


Figure 16 Calorimetric determination of the residual and configurational entropies of B₂O₃ glass and liquid. Data from [31].

Table 5 Residual entropies of oxide glasses determined from calorimetric measurements performed between 0 K and the melting point of the stable crystal.

Oxide	$S_g(0)$ J/mol K	$S_g(0)$ J/g atom K
B ₂ O ₃	11.2	2.2
GeO ₂	6.6	2.2
SiO ₂	5.1	1.7
Na ₂ SiO ₃ ^a	5.11	0.8
K ₂ Si ₂ O ₅ ^a	18.0	2.0
K ₂ SiO ₃ ^a	12.6	2.1
CaSiO ₃	8.8	1.8
CaMgSi ₂ O ₆	23	2.3
MgSiO ₃	11.2	2.2
Mg ₂ SiO ₄ ^a	7	1.0
NaAlSiO ₄	9.7	1.4
NaAlSi ₃ O ₈	36.7	2.8
KAlSi ₃ O ₈	28.3	2.2
CaAl ₂ Si ₂ O ₈	36.8	2.8
Mg ₃ Al ₂ Si ₃ O ₁₂	56.3	2.8
Mg ₂ Al ₄ Si ₅ O ₁₈	94	3.2

^a Unpublished, less accurate derivation.

Source: Data from per mol or reported to the number of atom (g atom) [19].

why available data are rather scarce (Table 5). Of particular interest is the result obtained for NaAlSiO₄ whose residual entropy is smaller than that of SiO₂, on a g atom basis (i.e. per atom). Both glasses are made up of a continuous, open network of TO₄ tetrahedra whose purely topological entropies should not be widely different. The lower entropy of NaAlSiO₄ was, therefore, indicating a highly ordered Al–Si distribution, which has later been confirmed by NMR measurements [19]. That residual entropies determined from calorimetric experiments are thus making physical sense is also confirmed, among other examples, by the very low value calculated for Mg₂SiO₄ whose extremely poor vitrifiability may be assigned to the very rapid rate at which configurational entropy is lost [40].

More generally, the validity of the concept of residual entropy for glasses is also illustrated by a different approach based on Adam–Gibbs theory of relaxation processes. From the postulated proportionality between relaxation times and configurational entropy, S^{conf} , one finds that the viscosity is given by [41]

$$\log \eta = A_e + B_e / TS^{\text{conf}}, \quad (14)$$

where A_e is a pre-exponential term and B_e a parameter proportional to the Gibbs-free energy barriers opposing viscous flow. Because the temperature dependence of S^{conf} can be calculated with Eq. (11) and

$$S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + \int_{T_g}^T \frac{C_p^{\text{conf}}}{T} dT, \quad (15)$$

these expressions represent a three-parameter equation for viscosity. From fits made with Eqs. (13) and (14) to data spanning wide intervals from the glass transition range to superliquidus temperatures, one then derives the A_e and B_e parameters and the residual entropy at the relevant glass transition temperature. The strikingly good agreement of these values with the values determined by calorimetric experiments thus validates the whole approach (Figure 17), which is especially useful as there is no other experimental method available for determining configurational entropies.

For hyperquenched glasses, however, very high fictive temperatures can affect entropy significantly. Provided that the fictive temperatures and relevant heat capacities are known, the entropy difference between glasses with different thermal histories is readily accounted with

$$S_g^{\circ}(0)_2 - S_g^{\circ}(0)_1 = \int_{T_{f1}}^{T_{f2}} \frac{C_{p1}^{\circ} - C_{pg}^{\circ}}{T} dT \approx (C_{p1}^{\circ} - C_{pg}^{\circ}) \ln \left(\frac{T_{f2}}{T_{f1}} \right). \quad (16)$$

As recently discussed [42], this effect could be the reason why glass fibers dissolve much more rapidly than bulk glass pieces in aqueous solutions.

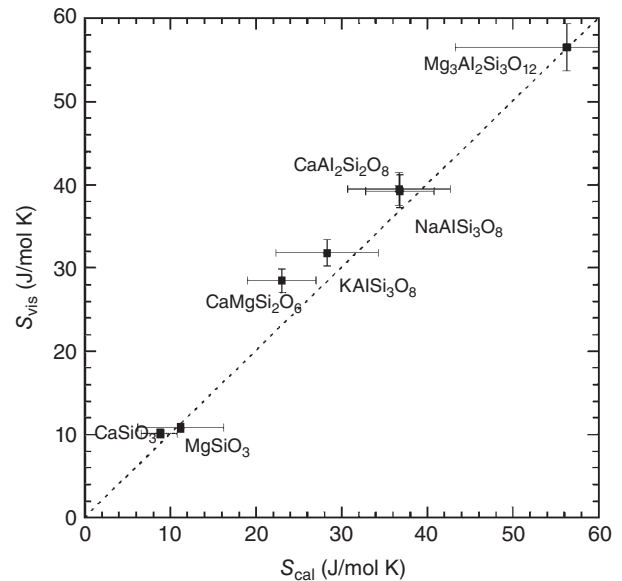


Figure 17 Comparison between residual entropies derived from calorimetric and viscosity measurements. Data sources in [19].

5 Reaction Thermodynamics

5.1 Enthalpies of Mixing

In a solution, the Gibbs free energy is the weighted sum of the chemical potentials μ_i of the components

$$G = \sum x_i \mu_i = \sum x_i \mu_i^\circ + \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}, \quad (17)$$

where x_i is the mole fraction of component i and ΔH_{mix} and ΔS_{mix} are the enthalpies and entropies of mixing, respectively. As already alluded to, ΔH_{mix} can be determined by solution calorimetry from the measurements made on the end-members and other compositions of the system of interest. Even when if one considers only binary or pseudo-binary joins, the number of relevant glass-forming systems is so large that the data available for some tens of joins [18] represent but a small fraction of those that would be worth investigating. Hence, the important Al–Si substitution for a number of alkali and alkaline earth cations will serve here to illustrate a few salient points [43].

These results are plotted as negatives of enthalpies of solution to reflect directly the enthalpy scale (Figure 18). Enthalpies of mixing between SiO_2 and $\text{M}_{x/2}\text{AlO}_2$ SiO_2 are negative in all systems, which attest to strong affinity between these components. The enthalpy minimum lies near 50 mol % with a depth that increases with the field strength of the M-cation from +10 to below -20 kJ/mol from Mg- to K-aluminosilicates and the relative extent of freezing-point depressions at eutectic points. Although they are directly relevant to phase equilibria, these data require the aforementioned fictive-temperature corrections for use in Eq. (17). For samples whose glass transition temperatures are higher

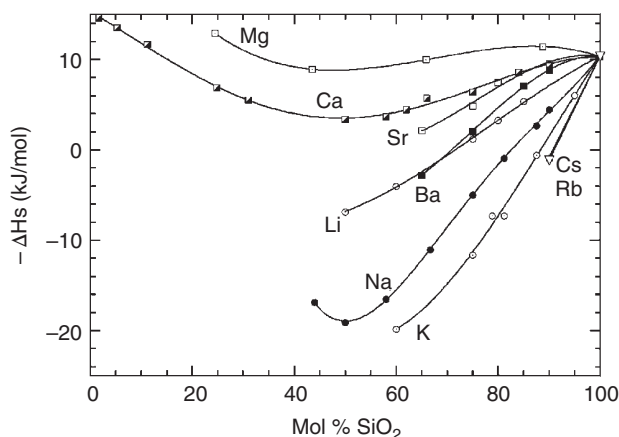


Figure 18 Enthalpies of solution of aluminosilicate glasses along binary joins. Data from [43].

than 700°C , the temperature of solution calorimetry, the adjustments can amount to 5 kJ/mol or more [21] to determine accurately enthalpies of mixing between SiO_2 and the most SiO_2 -poor composition investigated for a given system.

5.2 Gibbs Free Energies of Formation

As a rule, mixing of individual oxides in glass-forming systems is highly nonideal in terms of both enthalpy and entropy factors (Chapter 5.3). Because atomic interactions are essentially of a binary nature (Chapter 2.8), however, mixing of two binary systems is much less non-ideal, and so on when the chemical complexity keeps increasing. In thermodynamic modeling, it is thus advantageous to select as components not the relevant oxides but more complex entities in which the main interactions are already embodied [44]. In a given system, a natural choice then is to select for a particular composition the phases constituting the stable crystalline assemblage indicated by the phase diagram, between which the mixing enthalpies and entropies are negligibly small compared with those of the constituting oxides. In this way, a given property Y of a glass or its melt is simply approximated by the sum

$$Y = \sum x_i \cdot Y_i, \quad (18)$$

where x_i is the mol fraction of constitutional phase i and Y_i is its partial molar property, which is assumed to be independent of composition.

Taking the enthalpy of a glass at room temperature as an example, one obtains the H_i values from the available enthalpies of formation of ΔH_{fi}° of the i th crystalline phase and its enthalpy of vitrification ΔH_{vi} , i.e. $H_i = \Delta H_{fi}^\circ + \Delta H_{vi}$. If ΔH_{vi} data are lacking, then the approximation $\Delta H_{vi} \approx \Delta H_{mi}/2$ may be used. For entropies, the other rule of thumb $\Delta S_v \approx \Delta S_{mi}/3$ applies. If a glass melt above liquidus temperature is considered, the procedure is the same except that the H_i values refer to the liquid state.

To select the right set of components, use is made of the fact that in most systems of natural or industrial interest four oxides make up at least 85% of the composition and that stoichiometric compounds rarely bear more than three different oxides. Thus, the major four oxides are allotted according to existing phase diagrams while the rest is determined by normative geochemical calculations. On this basis, the composition of a complex system can be expressed unambiguously [45]. The major advantage of the method thus is that no structural information at all is needed as long as multicomponent systems (ternary and beyond in terms of oxides) are dealt with. Its usefulness is apparent in Table 6 where excellent agreement is found between the experimental and model

Table 6 Determination of the Gibbs free energies of formation from the oxides for a few glasses from calorimetric and viscosity measurements. Data in wt % and kJ/mol^a.

Oxide	V1	V2	V3	V4
SiO ₂	42.10	42.8	42.4	44.7
Fe ₂ O ₃	6.20	5.25	8.0	7.4
Al ₂ O ₃	20.02	24.0	21.3	21.0
CaO	13.2	12.25	15.25	9.11
MgO	5.03	4.02	10.2	5.0
Na ₂ O	13.5	11.7	2.83	12.85
T_g	892.6	924.3	958.9	902.4
$C_p^g(T_g)$	25.46	25.43	25.37	25.36
A_e	-1.4755	-1.02	-2.68	-1.09
B_e	90.379	79.283	138.670	84.704
$S^{\text{conf}}(T_g)$	7.00	6.11	9.22	6.66
ΔS_0	5.06	5.11	4.41	4.99
$S(T_g) - S_0$	36.80	32.76	44.43	52.56
ΔH_f°	-40.69	-33.86	-9.76	-32.29
$\Delta G_f^\circ(\text{exp})$	-44.14	-33.98	-35.43	-12.94
$\Delta G_f^\circ(\text{calc})^b$	-41.4	-35.0	-37.0	-10.6

^a Experimental data from an unpublished report prepared at IPGP by D. Brisart; solution calorimetry at 973 K in lead borate done with J. Rogez at the TECSEN laboratory (CNRS, Marseilles).

^b [45].

values of the Gibbs free energies of formation of four glasses.

6 Perspectives

That physical properties can represent a valuable source of structural information is often overlooked. Structures are determined by thermodynamics, and not the other way around. Despite any structural complexities of the amorphous state, an important simplifying feature is that properties of glasses generally vary smoothly with composition, without all the irregularities displayed by those of crystals caused by the constraints imposed by the specificities of discrete crystal structures. In other words, structural conclusions drawn from a few amorphous compositions can in general be extended readily to a much wider composition range than can be done for crystalline materials.

The conclusions are the most straightforward for solids when properties are vibrational in origin. Difficulties are much greater for liquids whose variety of mechanisms involved in temperature-induced structural changes remain elusive in spite of the enormous amount of

structural information that is being gathered with a variety of techniques [19]. The contrast with the scarcity of thermodynamic data at temperatures much higher than 1000 K is striking. Additional measurements are thus needed but the lack of commercially available high-precision equipment is a real impediment that could last and affect progress to be made either for tailoring new materials or for understanding igneous processes at all relevant scales.

A really fundamental goal will be to integrate into a consistent framework the structural and thermodynamic aspects in a way consistent with the fact that decreasing energy scales correlate with increasing interaction length scales. Recent work on melting mechanisms illustrates this kind of approach [46]. The starting point is the correlation observed between the calorimetric premelting effects displayed by Na₂SiO₃ and Li₂SiO₃ (Figure 2) and changes in the Raman spectra pointing, without significant enthalpy effects, to the production of mobile Na⁺ ions and Si—O[−] moieties that remain part of the crystalline silicate chains as negatively charged Q² species; these species then react with “normal” Q² units to cross-link the chains with Q³ species, liberating along the way “free” oxygen O^{2−} ions. Actual melting finally takes place with a sharp enthalpy change through depolymerization of silicate chains by free O^{2−} ions to form Q¹ species also observed spectroscopically, whereas the same reactions proceed in the reverse order upon crystallization.

Another field where much remains to be done is high-pressure experiments or, at least, measurements on permanently densified glasses, which are of fundamental interest in geophysics and are also catching the physicists' attention. The few available data for the pressure dependence of the enthalpy (Table 7) indeed suggest that strong composition-structure effects are also to be revealed. For completeness, one must also recall that thermodynamic and volume (Chapter 3.5) properties are closely related through the pressure derivative of the Gibbs free energy, $(\partial G/\partial P)_T = V$. Any progress made on the equations of state of melts will thus be of immediate relevance to high-pressure thermodynamic properties.

Table 7 Variations of the enthalpy (kJ/mol) of oxide glasses with the density (g/cm³).

Glass	$(\partial H/\partial \rho)_T$
GeO ₂	-32.3 (14.1)
SiO ₂	-44 (20)
K ₂ Si ₄ O ₉	-105.2 (10.7)
Na ₂ Si ₄ O ₉	-52.1 (13.6)
NaAlSi ₃ O ₈	-9.1 (10.4)

Source: Data from [47].

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3.7

Structural and Stress Relaxation in Glass-Forming Liquids

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1 Introduction

An essential feature of the glassy state is the existence of configurational degrees of freedom. Both the number and the occupational state of these configurational degrees of freedom have an enormous impact on macroscopic properties such as the refractive index or the specific enthalpy and volume. Most of the configurational degrees of freedom may be considered as frozen-in below the glass transition range on any realistic timescale. If reheated into this temperature range, however, glass will undergo *structural relaxation*, i.e. the occupational state of these degrees of freedom will change which is equivalent to changes of the atomic structure. These changes will tend to minimize Gibbs free energy at the environmental temperature and they will have the impact on macroscopic properties mentioned above.

A good example of structural relaxation is the thermal shrinkage observed when glass is reheated to temperatures just below the glass transition. Said change of the specific volume is of particular importance for, e.g. high-temperature coating processes. Similarly, structural relaxation leads to what is called *refractive index drop* in precision molding of lens elements. A straightforward way to observe the glass transition range is by differential scanning calorimetry – calorimetric glass transition, see Section 3.5). In addition, glass will use this reconfiguration capability to undergo stress relaxation, i.e. time-dependent yielding to an imposed stress by viscous flow.

In this chapter, the above examples will be presented in detail to illustrate the practical relevance of structural relaxation. Then, the concept of fictive temperatures will

be introduced. At constant temperature and pressure, the time-dependence of the physical properties of a relaxing material indicates that other variables have to be defined to describe its state. This is done with fictive temperatures, which are the basis of the various models that account for the kinetics of structural relaxation. Stress relaxation is the other topic. In the transition range, the mechanical high-temperature response of glass – like a viscous liquid – and the mechanical low-temperature response – like an elastic solid – coexist. Their combined effect is called viscoelasticity: when glass is exposed to strain, stress will occur as an initial response, and this stress will subsequently decrease over time due to the above reconfiguration mechanism. There are two fundamental viscoelastic cases, the constant volume one (shear) and the constant shape one (pressure), which will both be discussed at the end of the chapter.

2 Structural Relaxation: A Few Examples

As it has already been said, the classical example of structural relaxation is the linear dependence of the refractive index on the logarithm of the cooling rate [1]. The slope is proportional to the number of configurational degrees of freedom, the occupational state of which is determined by the cooling rate. This issue will be discussed in more detail.

A second example is prestressing or toughening of glass plates (Figure 1), which hinges on viscous flow upon processing but is also influenced by the differing occupational states of the configurational degrees of freedom at the glass surface and in the glass core [2–4].

When heated above the glass transition range and then rapidly cooled, a glass plate develops a temperature gradient such that the temperature is highest in its core and

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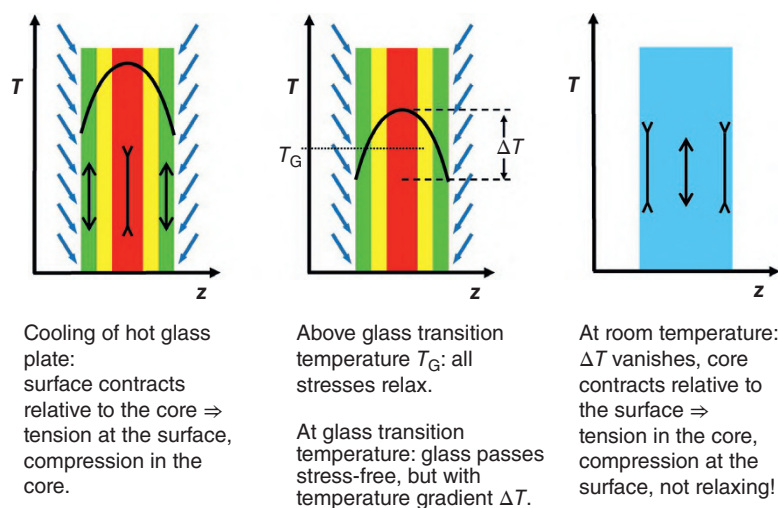


Figure 1 Prestressing/toughening of a glass plate.

lowest at its surface. As a consequence, the surface contracts relative to the core, which results in compressive stress in the core and tensile stress at and near the surface. At temperatures above the glass transition range, these stresses relax by viscous flow. Therefore, the glass plate passes this range stress-free during further cooling, but with a (high) internal temperature gradient that gradually diminishes and finally disappears at room temperature. As a consequence, the core contracts relative to the surface, which results in tensile stress in the core and desirable compressive stress at the surface. These stresses are permanent and increase fracture toughness – as long as the glass plate is not reheated to the glass transition range.

Most of the contraction of the surface relative to the core and, then, of the core relative to the surface is due to thermal expansion. There is, however, a secondary effect due to said differing occupational states of the configurational degrees of freedom at the surface and in the core. As already stated, the occupational state of the latter depends on the cooling rate. The higher the cooling rate, the more high-energy states are occupied and vice versa. As the high-energy states are more space consuming than the low-energy ones, said secondary effect due to thermal expansion results. Owing to the comparatively low thermal conduction in glass, the cooling rate is much faster at the surface than in the core during prestressing. This results in an inhomogeneous distribution of occupational states over the plate cross-section, and in return in an additional contribution to the final contraction of the core relative to the surface.

The third example is the peak of the absorption curve of silicate glasses [5] in the Gigahertz/Terahertz range, which is a typical feature of all glass-forming systems, the so-called Boson peak. Its intensity is sensitive on the cooling rate and, thus, on the occupational state of the configurational degrees of freedom [6]. Hence, it is the relaxational state that eventually determines the course of the absorption curve in this frequency regime.

3 Structural Relaxation

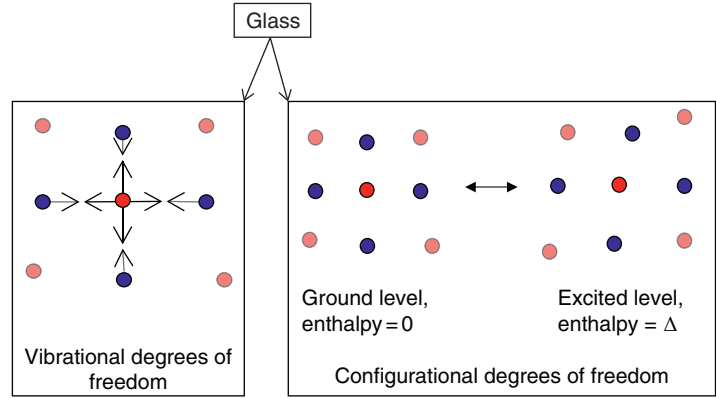
3.1 Description of the Configurational State by at Least One Fictive Temperature

Usually one or more order parameters or one or more fictive temperatures (Sections 3.2–3.4) are selected to quantitatively describe the configurational state of a glass and, thus, the response of the macroscopic properties to its changes [7, 8a]. The basic idea is to take temperature as what it is in terms of thermodynamics, i.e. a distribution parameter indicating the average excitation level of every degree of freedom belonging to the thermal reservoir considered. If one makes a *Gedankenexperiment* (thought experiment) distinguishing between two thermal reservoirs consisting of degrees of freedom that are either all vibrational or all configurational (Figure 2), then one must also distinguish between two temperatures [9–11]. The first is the common temperature; the second is the distribution parameter describing the average excitation level of the configurational degrees of freedom, which is called fictive temperature.

If enough thermal energy is exchanged with the environment at a high enough rate, the vibrational and environmental temperatures are equal. If, in addition, there is also sufficient energy exchange between the vibrational and configurational degrees of freedom, complete thermal equilibrium is achieved and the temperature is uniform.

Regarding kinetics, the equilibration of vibrational and configurational degrees of freedom is a thermally activated process. What is called *glass transition range* is the temperature interval where, upon cooling, thermal activation is no longer large enough for ensuring equilibration and instead becomes too small for making equilibration possible on any realistic timescale. For the fictive temperature, this means that it remains equal to the environmental temperature above the glass transition but is frozen in at a constant value below it. This value is

Figure 2 Imaginary separation of glass into two thermal reservoirs containing either the vibrational degrees of freedom (occupation number $\propto \exp(-i \cdot h\nu/kT)/Z$, $i = 1, \dots, \infty$, ν vibrational frequency, h Planck's constant, $Z = \sum \exp(-i \cdot h\nu/kT)$ partition function for one vibrational degree of freedom) or the configurational degrees of freedom (for the two state examples shown here: occupation number ground level $\propto 1/Z'$, occupation number upper level $\propto \exp(-\Delta/kT)/Z'$, $Z' = 1 + \exp(-\Delta/kT)$ partition function).



determined by the actual equilibration kinetics and the applied cooling rate.

A shortcoming affects the description of the configurational state of a glass with a single fictive temperature, however, because this picture implicitly assumes strong coupling, i.e. an intense exchange of energy, between all configurational degrees of freedom to ensure that their average excitation levels follow a single distribution parameter. Coupling between configurational degrees of freedom is only indirect, however, because there is no direct energy transfer path between them. Rather, this energy transfer involves the vibrational degrees of freedom as mediator and runs this way: one configurational degree of freedom – vibrational degrees of freedom – other configurational degree of freedom. Thus, the coupling between the configurational degrees of freedom depends on the excitation level of the vibrational degrees of freedom so that it is subject to thermal activation itself.

Therefore, a set of fictive temperatures is required for the description of the configurational state of a glass. In other words, the thermal reservoir containing the configurational degrees of freedom must be split into a number of sub-reservoirs, each having a fictive sub-temperature as a distribution parameter. From a theoretical standpoint, this change makes the concept less satisfactory than expected, but it has the major advantage of leading to very useful quantitative predictions of certain glass properties.

3.2 Prediction of Glass Properties from Temperature and Fictive Temperature(s)

Such quantitative models first rely on the assumption that vibrational state and configurational states may be separated, i.e. that changes in macroscopic properties such as the enthalpy H or the volume V of a glass sample of mass M may be split into a vibrational and a configurational part and thus be written:

$$\begin{aligned} dH &= dH^{\text{vib}} + dH^{\text{conf}} \\ dV &= dV^{\text{vib}} + dV^{\text{conf}} \\ &\dots \end{aligned} \quad (1)$$

The second assumption is that any macroscopic property responds linearly to infinitesimal changes in both the environmental and the fictive temperatures:

$$\begin{aligned} dH/M &= c_p^{\text{vib}} \cdot dT + c_p^{\text{conf}} \cdot dT_f \\ dV/V &= 3\alpha^{\text{vib}} \cdot dT + 3\alpha^{\text{conf}} \cdot dT_f \end{aligned} \quad (2)$$

(one fictive temperature)

...

or

$$\begin{aligned} dH/M &= c_p^{\text{vib}} \cdot dT + c_{p,1}^{\text{conf}} \cdot dT_{f,1} + \dots + c_{p,n}^{\text{conf}} \cdot dT_{f,n} \\ dV/V &= 3\alpha^{\text{vib}} \cdot dT + 3\alpha_1^{\text{conf}} \cdot dT_{f,1} + \dots + 3\alpha_n^{\text{conf}} \cdot dT_{f,n} \end{aligned} \quad (3)$$

(n fictive sub-temperatures)

...

where c_p is the specific heat at constant pressure and α the linear coefficient of thermal expansion (3α = volume coefficient of thermal expansion) [8a].

For convenience, one writes in the case of n fictive sub-temperatures:

$$\begin{aligned} dH/M &= c_p^{\text{vib}} \cdot dT + c_p^{\text{conf}} \cdot (v_1 \cdot dT_{f,1} + \dots + v_n \cdot dT_{f,n}), \\ v_i &= \frac{c_{p,i}^{\text{conf}}}{c_p^{\text{conf}}}, \quad c_p^{\text{conf}} = \sum_{i=1}^n c_{p,i}^{\text{conf}} \\ dV/V &= 3\alpha^{\text{vib}} \cdot dT + 3\alpha^{\text{conf}} \cdot (v_1 \cdot dT_{f,1} + \dots + v_n \cdot dT_{f,n}), \\ v_i &= \frac{\alpha_i^{\text{conf}}}{\alpha^{\text{conf}}}, \quad \alpha^{\text{conf}} = \sum_{i=1}^n \alpha_i^{\text{conf}} \\ &\dots \end{aligned} \quad (4)$$

and may also define a weighted mean value of the fictive sub-temperatures by

$$T_f := \sum_{i=1}^n v_i \cdot T_{f,i}. \quad (5)$$

where the v_i coefficients are assumed to be the same. In this manner, one obtains [8a]:

$$\begin{aligned} dH/M &= c_p^{\text{vib}} \cdot dT + c_p^{\text{conf}} \cdot dT_f \\ dV/V &= 3\alpha^{\text{vib}} \cdot dT + 3\alpha^{\text{conf}} \cdot dT_f \end{aligned} \quad (6)$$

Note that a change dT_f of this weighted mean (and any resulting change dH , dV , or anything else) may be caused by different sets of $dT_{f,i}$ leading to the same $dT_f = \sum v_i dT_{f,i}$. Together with a kinetic model for the fictive temperature(s), Eqs. (2), (3) and the following ones allow macroscopic properties like enthalpy and volume to be calculated from the thermal history of the glass.

At this point, one should inquire why the v_i coefficients are the same for H , V , and other macroscopic properties. As a matter of fact, whether the kinetics of H , V , or other macroscopic properties (e.g. refractive index) is related to one fictive temperature or to one set of fictive sub-temperatures has been debated extensively. With respect to all types of glass-forming systems, including polymers, the former alternative does not seem to be correct (as pointed out by, e.g. [12]), although the differences between the two are small (e.g. [13]). For silicate glasses, however, this universality seems to exist [14]. All examples given below do support this view that the kinetics of all macroscopic properties are related to a single fictive temperature or a single set of fictive sub-temperatures. To ensure a fair comparison of differently obtained kinetic data, an appropriate deconvolution of, e.g. DSC data has to be carried out (see Section 3.5).

Note that, the timescales of the vibrational and configurational responses to a jump in a state variable are essentially different. For an instantaneous temperature jump ΔT (at $t = 0$ for simplicity), there will first be an almost instantaneous change in vibrational states causing an enthalpy change $c_p^{\text{vib}} \Delta T$, followed by a time-dependent variation of the configurational state. The resulting enthalpy change is given by $c_p^{\text{conf}}(T_f(t) - T_f(0))$ at any time $t > 0$. The actual value of $T_f(t) - T_f(0)$ depends on kinetics. At some temperature below the glass transition range, the time to equilibrate vibrational and configurational degrees of freedom will become immeasurably long and $T_f(t) - T_f(0) = 0$ will hold on any realistic timescale. Only for $t \rightarrow \infty$ the system will eventually equilibrate and $T_f(\infty) - T_f(0) = \Delta T$ will hold.

Accordingly, the fictive temperature of a glass sample cooled from temperatures in or above the glass transition range to temperatures significantly below will reach an effectively final value that will not experience appreciable change on any realistic timescale (i.e. for $t < \infty$!). This value is called the glass transition temperature T_G . As T_G depends on the cooling rate, or more generally, the

thermal history, one may also define of T_G in a unique sense referring to the value obtained from glass linearly cooled at 2 K/min. It is determined by dilatometry according to ISO 7884-8 [15].

3.3 Tool's Original Model

The concept of fictive temperature as well as the first step toward a model of glass relaxation were proposed by Tool in 1946 [7] in terms of a structural relaxation time τ . The rate equation describing the kinetics of a single fictive temperature T_f was expressed with an Arrhenius-type *Ansatz* (approach)

$$\frac{dT_f}{dt} = \frac{T - T_f}{\tau}, \quad \tau = \tau_0 \cdot e^{H/R \cdot T} \quad (7)$$

where R is the gas constant. The basic ideas of this *Ansatz* are that:

- 1) the system tends to equilibrate, i.e. $T_f = T$, with a driving force given by the difference $T - T_f$.
- 2) the system is configurationally trapped in a *potential cage* where it vibrates at a frequency $\nu = 1/\tau_0$; a move toward another configuration then requires a jump over an enthalpy barrier H .

With these assumptions, H should be of the order of magnitude of the dissociation energy of a network, for example, that required to break all oxygen bridges. Since configurational rearrangements involve cooperative motion of numerous atoms rather than hopping of individual ones only, H is usually considerably higher than the enthalpy required for overcoming a microscopic barrier. For polymer glasses, H may actually exceed the dissociation energy of the C—C bond by half an order of magnitude [16].

Concerning ν , one is tempted to identify it with the Einstein frequency or another typical frequency of atomic vibrations. One finds, however, that the high values found for H have to be associated with either very high ν or very low τ_0 values to make, with Tool's formalism, the glass transition occur in the experimentally observed range, i.e. at several hundred rather than at several thousand degrees.

To assess the applicability of Eq. (7), one may have a glass equilibrate at a temperature T_0 first and then make a temperature jump from T_0 to T at $t = 0$. In that case, the fictive temperature for $t > 0$ is given by the differential Eq. (7) for constant temperature and for the initial condition $T_f(0) = T_0$. The solution is the well-known single-exponential relaxation function:

$$T_f = T + (T_0 - T) \cdot e^{-t/\tau} \quad (8)$$

However, more sophisticated approaches have had to be developed, since neither enthalpy nor volume relaxation conforms to such a simple solution.

3.4 The Tool–Narayanaswamy–Moynihan Model

This model is commonly known as Tool–Narayanaswamy or Tool–Narayanaswamy–Moynihan since its nonlinear character was dealt with by Narayanaswamy [17] and Moynihan [18]. As Mazurin, Rekhson, and Startsev had independently come to the same results [19] and as Kohlrausch-type kinetics had been introduced by Mazurin and Rekhson [20], it is appropriate to follow Hodge's [21] suggestion and term it Tool–Narayanaswamy–Moynihan(–Mazurin–Rekhson–Startsev), or TNM(MRS) model for short. Two main facts have motivated its introduction:

- 1) The configurational response of enthalpy or volume (or any other macroscopic property) to a temperature jump after equilibration is not by a single but by a stretched exponential, i.e. H or V (or another property) approximately follow a so-called Kohlrausch(–Williams–Watts)–function $\exp[-(t/\tau)^b]$, $0 < b < 1$ [22, 23] as also does a calculated fictive temperature (Figure 3).
- 2) Particularly for large temperature jumps, one observes an asymmetry between the upward and downward temperature jumps to the same final temperature. If prior equilibration was at a higher temperature, relaxation is faster and vice versa. The famous density relaxation experiments by Hara and Suetoshi [24] illustrate this behavior (Figure 4).

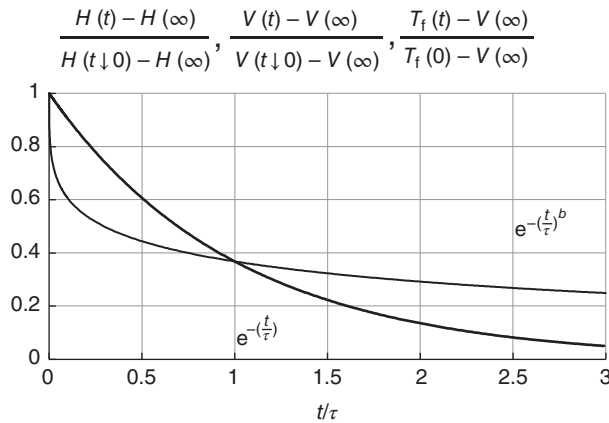


Figure 3 Single exponential $\exp(-t/\tau)$ versus stretched exponential $\exp(-(t/\tau)^b)$, $b = 0.3$. $H(t \downarrow 0)$, $V(t \downarrow 0)$ denote the values H , V take after the instantaneous vibrational response to the temperature jump, i.e. only the time-dependent configurational response is shown.

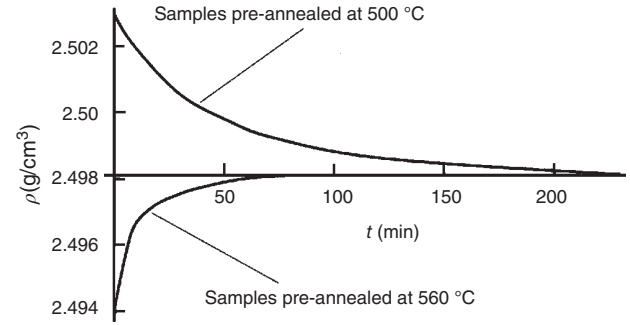


Figure 4 Density measurements of Hara and Suetoshi on soda-lime-glass during annealing at 530 °C.

These two facts are allowed for by the TNM(MRS) model in the following way:

- 1) The configurational state of a glass is described by a distribution of fictive sub-temperatures rather than by a single fictive temperature. By *fictive temperature*, without any further index, a weighted mean of the fictive sub-temperatures as defined in (5) is implied:

$$T_f(t) = \sum_{i=1}^n v_i \cdot T_{f,i}(t), \quad \sum_{i=1}^n v_i = 1 \quad (9)$$

- 2) All fictive sub-temperatures follow from the same type of differential equation as Tool's original one:

$$\frac{dT_{f,i}}{dt} = \frac{T - T_{f,i}}{\tau_i} \quad (10)$$

- 3) As a consequence, the isothermal relaxation of every fictive sub-temperature upon a temperature jump can be represented by a single-exponential (approximately, if ΔT is not too large, see below).
- 4) The coefficients v_i , relaxation times τ_i , and number n of fictive sub-temperatures are chosen such that the Kohlrausch-type response of the fictive temperature is best reproduced by the corresponding series of fictive sub-temperatures with single-exponential relaxation ("Prony-series"; with n given, the v_i and τ_i are found by an appropriate optimization routine):

$$\begin{aligned} T_f(t) &= T + (T_f(0) - T) \cdot e^{-(t/\tau)^b} \\ &= T + (T_f(0) - T) \cdot \sum_{i=1}^n v_i \cdot e^{-(t/\tau_i)} \\ &\equiv \sum_{i=1}^n v_i \cdot \left[T + (T_f(0) - T) \cdot e^{-(t/\tau_i)} \right] \\ &=: \sum_{i=1}^n v_i \cdot T_{f,i}(t) \end{aligned} \quad (11)$$

On the assumption of thermorheologic simplicity, b and, as a consequence, all v_i and quotients τ_i/τ are assumed independent of temperature.

- 5) The asymmetry of upward and downward temperature jumps is allowed for by the following modification of the thermal activation term:

$$\tau_i = \tau_{0,i} \cdot e^{(H/R) \cdot (x/T + (1-x)/T_f)} \quad (12)$$

where x is the so-called nonlinearity parameter that ranges from 0 to 1. If $x = 1$, Arrhenius behavior is obtained whereas $x < 1$ means that thermal activation is faster than with Arrhenius for $T_f > T$ and slower for $T_f < T$. In Eq. (12), T_f is the weighted mean from (9).

The deviation from Arrhenius-type thermal activation causes the differing forms of relaxation functions for small and large temperature jumps for which there is, or there is no, significant difference between Eq. (12) and $\exp(H/RT)$, respectively. As a consequence, the solutions to Eq. (10) are not single exponentials for large temperature jumps.

3.5 Calorimetric Determination of the TNM(MRS) Model Parameters

Differential scanning calorimetry [25] is a convenient technique to determine relaxation parameters (Figure 5). One measures the heat flux dH into a sample heated at ambient pressure and at constant rate dT/dt , which is commonly identified with $c_p^{\text{app}} \cdot dT$. Here, “apparent” means that any possible glass transition or crystallization is deliberately ignored. With respect to Eq. (6), one obtains:

$$c_p^{\text{app}} \frac{dT}{dt} := \frac{dH}{dt} = c_p^{\text{vib}} \frac{dT}{dt} + c_p^{\text{conf}} \frac{dT_f}{dt}. \quad (13)$$

Below the glass transition, the measured c_p values are purely vibrational whereas above it, they are also configurational. To distinguish between both contributions,

one may extrapolate c_p from below to above the glass transition with, for instance, the Einstein model and the Dulong–Petit-value as a high-temperature limit of c_p^{vib} .

In the glass transition range, the rapid variations of c_p^{app} reflect the fictive temperature(s) kinetics upon heating at a constant rate. From an analysis of this peak, the parameters of the TNM(MRS) model may be determined [26]. The procedure is as follows. From Eq. (13), one obtains:

$$\frac{dT_f}{dt} = \frac{c_p^{\text{app}} - c_p^{\text{vib}}}{c_p^{\text{conf}}} \cdot \frac{dT}{dt} \quad (14)$$

In an optimization routine, one calculates the left side of Eq. (14) from Eqs. (9), (10), and (12) and equates it to the right side by varying the parameters H , τ_0 , b , and x . In the first step of every optimization loop, a set of v_i and τ_i is calculated according to the optimization procedure already described with Eq. (11). The number n indicating the length of the “Prony Series” is individually picked and should be “sufficiently high.” In the example below, a value $n = 10$ is used.

To make sure that the parameters obtained from DSC are real and not adversely affected by unavoidable noise in the data, it is recommended to identify features like *peak width*, *peak-to-peak distance*, etc., that are very sensitive to a single parameter. One scan does not provide enough different features but two at different heating rates are in principle fine. These features are the position of the inflection point of the simulated c_p^{app} versus T curve, the width of the calorimetric glass transition, the shift of said inflection point with the heating rate, and the asymmetry of the glass transition, which are most sensitive to the parameters τ_0 , b , H/R , and x , respectively (Figure 6). Of course, an appropriate deconvolution of the DSC data is a prerequisite for achieving an excellent agreement between the calculated and experimental thermogram [27, 28].

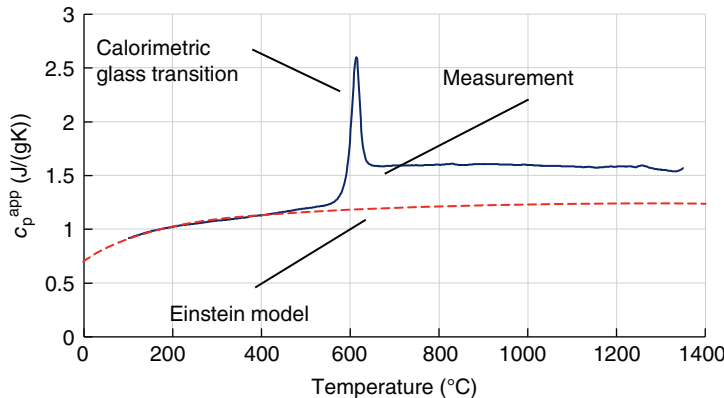


Figure 5 Typical DSC of an “optically” (i.e. slowly) cooled BK7 sample. Heating rate 12 K/min. Data as measured (no deconvolution). Measurement by SETARAM Multi-HTC 96® at the accredited laboratories of SCHOTT AG.

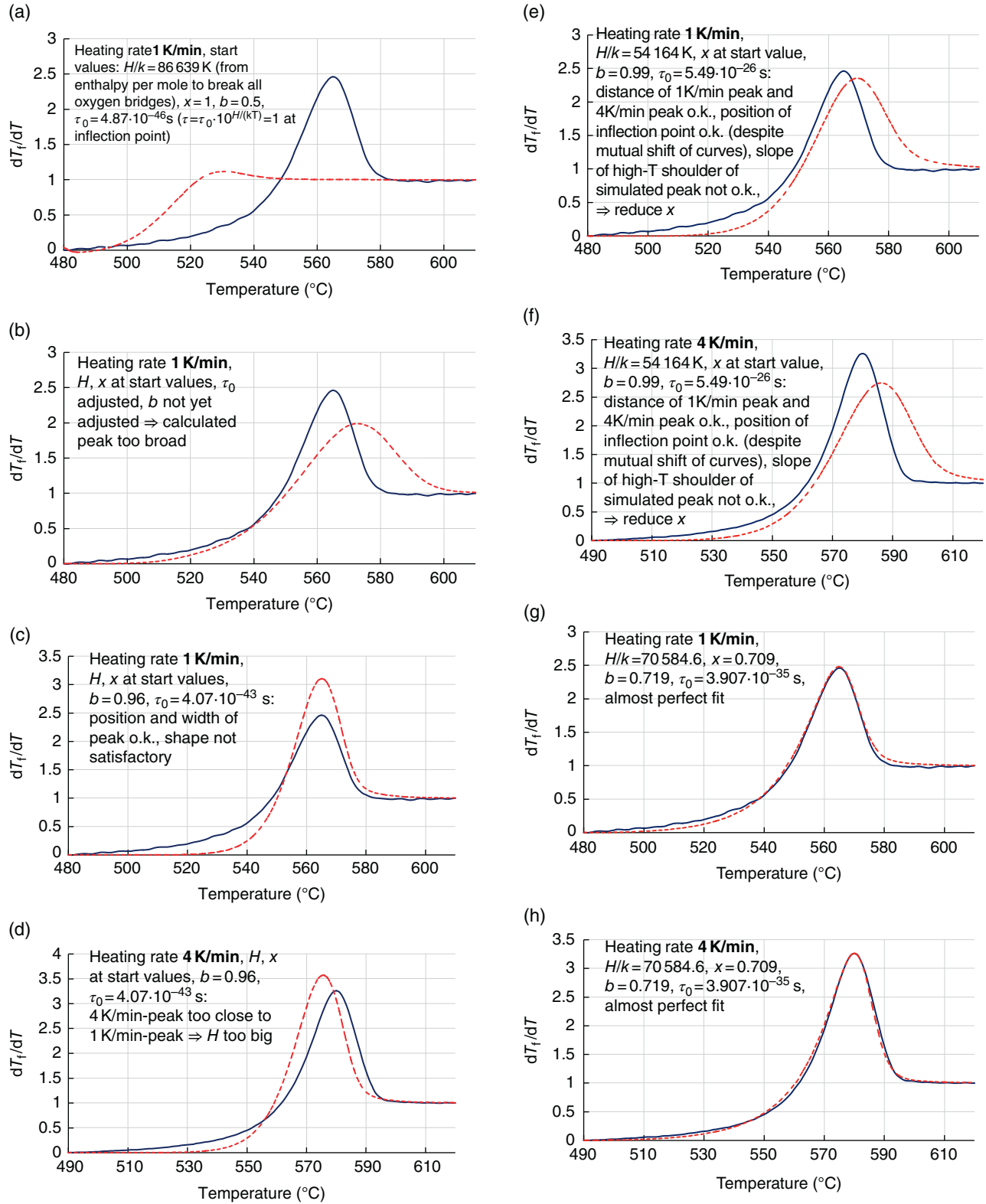


Figure 6 (a–h) Subsequent adjustment of the TNM(MRS) model parameters τ_0 , b , H/k , and x (adjustment of the latter not shown here) in order to make the simulated dT_f/dT curves (dashed lines) overlap with those obtained from measurement on BK7 (solid lines).

3.6 Prediction of Thermal Shrinkage with the TNM(MRS) Model

Once the parameters of the TNM(MRS) model are known, their predictive power can be ascertained from comparisons made between observed and calculated thermal shrinkage (Figure 7). In other words, the calorimetric TNM(MRS) parameters will be applied here to volume measurements. In these experiments, a temperature jump is simply realized through the transfer of a sample equilibrated in an oven at a given temperature to another oven at a different temperature. The glass can then be repeatedly removed from the latter at different times for length measurements at room temperature without any spurious influence of a dilatometer push rod. Provided that α^{conf} is known from a density measurement in the molten state, comparison of the measured values with TNM(MRS)-based calculations may be made without any fit parameter from

$$\frac{l(t) - l(t \downarrow 0)}{l(t \downarrow 0)} \equiv \frac{\Delta l}{l} = \alpha^{\text{conf}} \cdot (T_f(t) - T_f(0)). \quad (15)$$

Here on the left side is the relative shrinkage of the sample (as calculated from the measured sample length after a temperature jump at $t = 0$, the immediate response of the sample at $t = 0$ being discarded); and on the right side is the difference of the fictive temperatures at times t and 0.

Note that whereas these paragraphs deal with BK7®, similar recent investigations at Clemson University [29, 30] have dealt with the new glass N-BK7®.

3.7 Prediction of Refractive Index with the TNM (MRS) Model

The predictive power of the “calorimetric” TNM(MRS) model can again be demonstrated for an “optical”

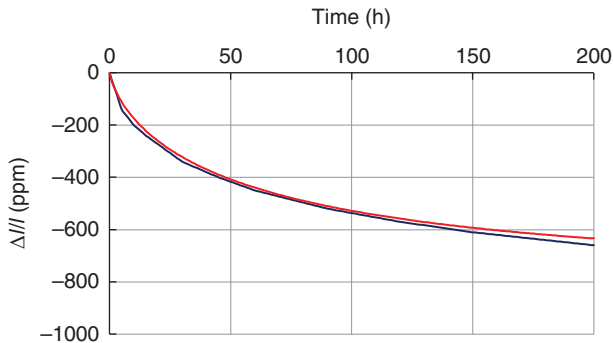


Figure 7 Comparison of a thermal shrinkage experiment on BK7 (solid line) with values calculated by the TNM(MRS) model (dashed line) with the parameters τ_0 , b , H/k , and x determined above and $\alpha^{\text{conf}} = 37$ ppm/K determined from a density versus temperature measurement in the molten stage. Measurement at the accredited laboratories of SCHOTT AG.

property, namely the refractive index with its dependence on a linear cooling rate [31]. Provided that the eigenfrequencies of the electron oscillators do not depend on thermal history, the refractive index is a function of density only, which in turn is a function of the fictive temperature. The room-temperature value of the latter depends on the cooling rate $q = dT/dt$. Therefore, one may write:

$$n(\lambda, q) = n(\lambda)_{\text{ref}} + \frac{\partial n(\lambda)}{\partial T_f} (T_f(q) - T_{f,\text{ref}}) \quad (16)$$

where λ is the wavelength, $\partial n/\partial T_f$ is assumed to be a constant, and “ref” refers to a reference state defined, for instance, by a standard cooling rate.

With the parameters of the TNM(MRS) model known from DSC and $\partial n/\partial T_f$ from an additional temperature-jump experiment, one may calculate $n(\lambda, q)$ from the reference value $n(\lambda)_{\text{ref}}$. For sake of simplicity, one may use an empirical linear relation from Moynihan and coworkers, which links the final fictive temperature and the logarithm of the cooling rate [18]:

$$\frac{H}{RT_{f,1}} - \frac{H}{RT_{f,2}} = \ln \left(\frac{q_2}{q_1} \right) \quad (17)$$

where $T_{f,1,2}$ is the fictive temperature upon linear cooling at a rate $q_{2,1}$. Although (17) has not yet been rigorously derived, it is widely applied because it condenses the essential result of the TNM(MRS) model in the case of linear cooling. Inserting (17) into (16) leads to:

$$n(\lambda, q) = n(\lambda)_{\text{ref}} + \frac{\partial n(\lambda)}{\partial T_f} \frac{T_f(q) T_{f,\text{ref}}}{H/R} \ln \left(\frac{q}{q_{\text{ref}}} \right) \quad (18)$$

For an approximation and further simplification, one may replace $T_f(q)$ and $T_{f,\text{ref}}$ with the T_G value according to [15]:

$$n(\lambda, q) = n(\lambda)_{\text{ref}} + \frac{\partial n(\lambda)}{\partial T_f} \frac{T_G^2}{H/R} \ln \left(\frac{q}{q_{\text{ref}}} \right) \quad (19)$$

Thus, the above-mentioned logarithmic relationship between the refractive index and the cooling rate may be derived from relaxation dynamics.

To calculate numbers, $\partial n/\partial T_f$, T_G , and H/R have to be known from the above-mentioned experiments ($\partial n/\partial T_f$ by V block refractometer measurement after annealing at different temperatures, i.e. by a temperature jump experiment; T_G , by dilatometry; H/R , by DSC plus data reduction according to the TNM(MRS) model). An overview of glass characterization methods is provided by [32]. The refractive index considered is n_d , i.e. the one at the helium d-line, 587.6 nm. For the crown glass P-SK57® and the flint glass P-LaSF47®, the values are given in Table 1 [31]. (N.B. For *crown* and *flint* glasses, see [33] and chapters 6.1 and 10.9).

Table 1 Properties of glasses P-SK57[®] and P-LaSF47[®].

Glass	$T_g/^\circ\text{C}$	$(\partial n_d/\partial T_g)/(1/\text{K})$	$(H/R)/\text{K}$
P-SK57 [®]	493	0.000 067 2	84 396.5
P-LaSF47 [®]	530	0.000 117	103 154

Table 2 Calculated versus measured refractive index values for glasses P-SK57[®] and P-LaSF47[®].

Glass	Cooling rate/ (K/h)	n_d (measured)	n_d (calculated)
P-SK57 [®]	2 (reference)	1.587 00	—
	9.5	1.586 26	1.586 27
	47	1.585 56	1.585 52
	236	1.584 85	1.584 77
P-LaSF47 [®]	2 (reference)	1.806 10	—
	9.6	1.805 03	1.804 95
	47	1.803 98	1.803 79
	230	1.802 89	1.802 63

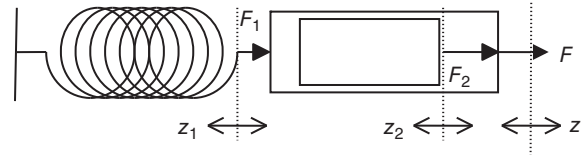
With the values from Table 1, one may calculate the refractive indices for different cooling rates and compare them with the measured ones, as provided in Table 2. Between the measured and the calculated values, one finds a maximum difference $<10^{-4}$ for glasses P-SK57[®] and $<3 \cdot 10^{-4}$ P-LaSF47[®], which is satisfactory with respect to the multiple error sources involved (temperature determination in the temperature jump experiment, calibration of the DSC, etc.).

4 Shear Viscoelasticity

Essentially, there are two orthogonal ways to deform a material, i.e. either at constant volume or at constant shape. Therefore, two types of viscoelasticity thus have to be dealt with. The first to be considered is the former, i.e. the response to shear stress.

4.1 Maxwell Model

If suddenly exposed to constant shear strain in the glass transition range, the glass will initially respond with elastic shear stresses, which will then decrease with time because of relaxation. As a consequence, the applied loads that maintain the constant shear strain will relax. If exposed to constant shear stress, the opposite will

**Figure 8** Maxwell model for viscoelasticity: spring in series with a dashpot (piston moving in a hollow cylinder filled with a viscous fluid). z_1 and z_2 , displacements of spring/piston; z , total displacement; $F_1 = F_2 = F$, force measured along the setup.

occur. In this case the glass will initially respond with an elastic shear strain, which in time will become a combination of the instantaneous response and a continuous elongation, which is referred to as creep. Maxwell has described these features by a model consisting of a spring and a dashpot in a series. Such a combination of an elastic response on short timescales and a viscous one on long timescales is called viscoelasticity [34a] (Figure 8).

For Maxwell's model and a continuously increasing elongation caused by a constant force F applied for $t \geq 0$, the following equation holds:

$$z = \frac{F}{D} + \frac{F}{\eta \cdot \frac{A}{d}} \cdot t \quad (20)$$

where D is the spring constant, η the viscosity, A both the outer surface of the piston and the inner surface of its hollow cylinder, and d the distance between the piston and hollow cylinder.

This equation may be derived with the following intermediary steps:

$$\begin{aligned} F_1 &= D \cdot z_1 \\ F_2 &= \eta \cdot \frac{A}{d} \cdot \frac{dz_2}{dt} \\ F_1 &= F_2 = F \\ z_1 + z_2 &= z \end{aligned} \quad (21)$$

The transition from elastic to viscous deformation occurs abruptly in this simplest case. In an infinitesimally short time, the elastic energy $\frac{1}{2}F^2/D$ accumulates in the spring and will be conserved for the rest of the time; the further energy transferred to the system will be completely dissipated.

Actual viscoelastic relaxation is observed if a constant elongation z is imposed. In this case, the force F required to maintain the elongation is:

$$F(t) = D \cdot \text{const} \cdot e^{-t \cdot (D \cdot d)/(\eta \cdot A)} = D \cdot \text{const} \cdot e^{-t/\tau} \quad (22)$$

The time constant $\tau = (A \cdot \eta)/(D \cdot d)$ is the relaxation time. Equation (22) may be derived with the following intermediary steps:

$$\begin{aligned}
\frac{dz_1}{dt} + \frac{dz_2}{dt} &= 0 \\
\frac{1}{D} \cdot \frac{dF_1}{dt} + \frac{d}{A} \cdot \frac{F_2}{\eta} &= 0 \\
F_1 &= F_2 = F
\end{aligned} \quad (23)$$

This time there is no further energy transfer to the system after the initial one. The elastic energy $\frac{1}{2}F^2/D$ accumulated in the spring at the beginning will not be conserved but will be dissipated completely in the dashpot during relaxation.

4.2 (Kelvin-)Voigt Model: Delayed Elasticity

For a more realistic description of viscoelasticity, delayed elasticity must also be taken into account. It may be represented by a (Kelvin-)Voigt model, which responds like a rigid body on a short timescale and like an elastic body on long timescales. The (Kelvin-)Voigt model consists of a spring and dashpot set up in parallel [34b] (Figure 9). For a constant force, the response is:

$$z = \frac{F}{D} \cdot \left(1 - e^{-t \cdot (d \cdot D)/(A \cdot \eta)}\right) \quad (24)$$

where the time constant involved is called retardation time. Equation (24) may be derived with the following intermediate steps:

$$\begin{aligned}
F_1 &= D \cdot z_1 \\
F_2 &= \eta \cdot \frac{A}{d} \cdot \frac{dz_2}{dt} \\
z_1 &= z_2 = z \\
F &= F_1 + F_2
\end{aligned} \quad (25)$$

From Eq. (25), one derives the following inhomogeneous differential equation that may be solved by the *variation of the constant*,

$$D \cdot z + \eta \cdot \frac{A}{d} \cdot \frac{dz}{dt} = F. \quad (26)$$

which leads to (24).

The case of an instantaneous, fixed elongation may not be simulated with a Voigt model.

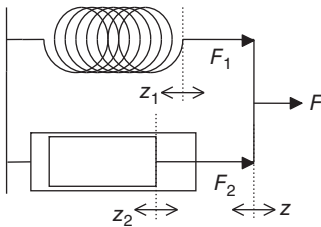


Figure 9 Voigt model for viscoelasticity: spring in parallel to a dashpot. $z_1 = z_2 = z$, displacement; F_1 , force measured at spring; F_2 , force measured at dashpot; F , total force measured.

4.3 Shear in Glass

When one considers a volume element under shear stress, the link between the glass response and that of the previous models is found by a transformation from force (elongation) to stress (strain) (Figure 10) as follows:

$$F_1 = D \cdot z_1 \rightarrow \sigma_1 = G \cdot \epsilon'_1 \quad (27)$$

$$F_2 = \eta \cdot \frac{A}{d} \cdot \frac{dz_2}{dt} \rightarrow \sigma_2 = \eta \cdot \frac{d\epsilon'_2}{dt} \quad (28)$$

where ϵ' is the amount by which the angle γ' changes. The quantity γ' in return is the change in angle between those two edges of the (previously cubic) volume element that are perpendicular to the shear axis.

Commonly, however, it is not ϵ' which is used to describe the deformation of the volume element, but the value ϵ which describes the change of the angle γ . γ is the angle between either of the above edges and the diagonal between them. As $\epsilon = \epsilon'/2$, one has to introduce a factor of 2 for compensation.

$$F_1 = D \cdot x \rightarrow \sigma_1 = G \cdot 2 \cdot \epsilon_1 \quad (29)$$

$$F_2 = \eta \cdot \frac{A}{d} \cdot \frac{dz_2}{dt} \rightarrow \sigma_2 = \eta \cdot 2 \cdot \frac{d\epsilon_2}{dt} \quad (30)$$

The simple Maxwell model allows an illustration of what is observed in glass

- 1) as short-term and long-term response to an imposed constant shear stress σ_0 :

$$\epsilon = \frac{\sigma_0}{2G} + \frac{\sigma_0}{2\eta} \cdot t = \left(\frac{1}{2G} + \frac{t}{2\eta}\right) \cdot \sigma_0 =: J(t) \cdot \sigma_0 \quad (31)$$

where $J(t)$ is the *compliance*,

the first term, i.e. $\sigma_0/(2G)$, describes the instantaneous response by the glass, which corresponds to the response of the spring in the simple Maxwell model; the second term, i.e. $\sigma_0/(2\eta)$, describes the continuous and constant deformation of the glass by creep, which corresponds to the response of the dashpot in the simple Maxwell model.

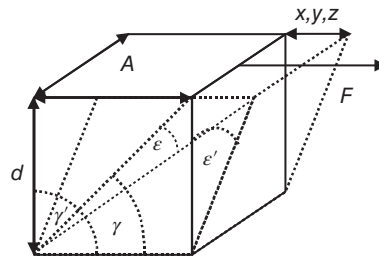


Figure 10 Definition of shear angle ϵ .

2) as response to a constant shear strain ε_0 :

$$\begin{aligned}\sigma(t) &= 2 \cdot G \cdot \varepsilon_0 \cdot e^{-t \cdot (G/\eta)} \\ &= (2 \cdot G \cdot e^{-t \cdot (G/\eta)}) \cdot \varepsilon_0 =: (2 \cdot G \cdot e^{-t/\tau}) \cdot \varepsilon_0 \\ &=: G(t) \cdot \varepsilon_0\end{aligned}\quad (32)$$

where $\tau = \eta/G$ is the relaxation time and $G(t)$ the time-dependent shear modulus (note $G(t) := 2 \cdot G \cdot e^{-t/\tau}$); the value $\sigma(0)$ describes the instantaneous response of the glass to the strain that is imposed at $t = 0$. So $\sigma(0)$ corresponds to the elastic response of the spring in the simple Maxwell model at $t = 0$ when the whole elongation is with the spring. The exponential decrease of $\sigma(t)$ describes the subsequent stress relaxation in the glass, which corresponds to the stress release in the spring when a rising fraction of the elongation is with the dashpot for $t > 0$.

The simple Voigt model allows the illustration of a delayed elastic response to constant shear stress:

$$\begin{aligned}\varepsilon &= \frac{\sigma_0}{2G} \cdot \left(1 - e^{-t \cdot (G/\eta)}\right) \\ &= \left(\frac{1}{2G} \cdot \left(1 - e^{-t \cdot (G/\eta)}\right)\right) \cdot \sigma_0 \\ &=: \left(\frac{1}{2G} \cdot \left(1 - e^{-t/\tau}\right)\right) \cdot \sigma_0 =: J(t) \cdot \sigma_0\end{aligned}\quad (33)$$

where $\tau = \eta/G$ is the retardation time and $J(t)$ again is the compliance. The delayed elastic response of the glass, i.e. a second elastic deformation gradually building up after the first, instantaneous elastic deformation, corresponds to the stress, which builds up in the spring of the simple Voigt model when the piston in the dashpot starts to move.

4.4 A Realistic Representation of Shear Relaxation: Burger Model

As shear relaxation of inorganic glasses cannot be described with either the Maxwell or the Voigt model alone (Figure 11), a better representation is provided by a combination of the two in series known as the Burger model [34c] (Figure 12). At constant stress, the strain is:

$$\begin{aligned}\varepsilon &= \left[\frac{1}{2G_2} + \frac{t}{2\eta_2} + \left(\frac{1}{2G_1} \cdot \left(1 - e^{-t \cdot (G_1/\eta_1)}\right) \right) \right] \cdot \sigma_0 \\ &=: J_{\text{Burger}}(t) \cdot \sigma_0\end{aligned}\quad (34)$$

The first term thus represents the instantaneous response, the second long-term creep, and the third delayed elasticity. At constant strain, the stress then is:

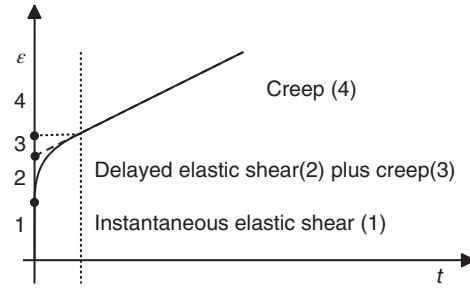


Figure 11 Typical time-dependent response of glass to constant shear stress. Essentially, there are phases. First, an instantaneous and reversible (i.e. elastic) strain response (1) when the shear stress is imposed at $t = 0$. Second, a transition phase involving both a reversible (i.e. elastic), however delayed strain contribution (2) plus an irreversible creep contribution (3). Third, pure creep (4).

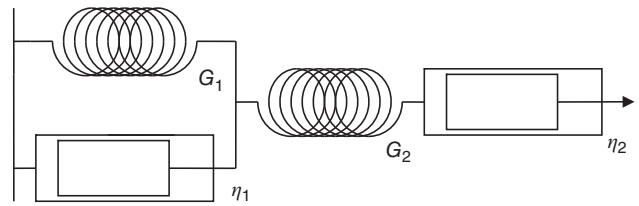


Figure 12 Burger model.

$$\sigma = \frac{2 \cdot G_2 \cdot \varepsilon_0}{(\lambda_+ - \lambda_-)} \cdot \left[\left(\lambda_+ + \frac{G_1}{\eta_1} \right) \cdot e^{\lambda_+ \cdot t} + \left(-\lambda_- - \frac{G_1}{\eta_1} \right) \cdot e^{\lambda_- \cdot t} \right] \quad (35)$$

This case is mathematically more complicated because the parameters λ_+ , λ_- are the roots of the equation $G_1 \cdot G_2 + (G_2 \cdot \eta_2 + G_1 \cdot \eta_2 + G_2 \cdot \eta_1) \cdot \lambda + \eta_1 \cdot \eta_2 \cdot \lambda^2 = 0$. See [34] or [35] for the derivations. Because λ_+ and λ_- are negative numbers, one may alternatively write:

$$\sigma = 2 \cdot G_2 \cdot \varepsilon_0 \cdot \left[v_1 \cdot e^{-t/\tau_1} + v_2 \cdot e^{-t/\tau_2} \right] \quad (36)$$

where τ_1 and τ_2 are relaxation times and v_1 and v_2 coefficients fulfilling the condition $v_1 + v_2 = 1$. As λ_+ is a small negative number compared with G_1/η_1 and λ_- is a large negative number compared with G_1/η_1 , both $v_1 = (\lambda_+ + G_1/\eta_1)/(\lambda_+ - \lambda_-)$ and $v_2 = (\lambda_- + G_1/\eta_1)/(\lambda_+ - \lambda_-)$ are positive numbers.

Thus, Eq. (35) or (36) is an analog of (32) with the difference that a single exponential relaxation in Eq. (32) has been replaced by a double exponential with two relaxation times.

As it will be shown below, the single exponential will be replaced with a whole spectrum of relaxation times in the general case.

4.5 Kohlrausch (Williams–Watts) Kinetics for Shear Relaxation

As for structural relaxation, replacement of single exponential functions with a stretched exponential or Kohlrausch(–Williams–Watts)-function is required to match the experimental data [8b] (Figure 13). For constant stress, the strain becomes:

$$\varepsilon = \left[\frac{1}{2G_0} + \frac{t}{2\eta} + \left(\frac{1}{2G_\infty} - \frac{1}{2G_0} \right) \cdot \left(1 - e^{-(t/\tau)^b} \right) \right] \cdot \sigma_0$$

$$=: J(t) \cdot \sigma_0 \quad (37)$$

where $1/(2G_0)$ represents the instantaneous elastic response, $1/(2G_\infty)$ the sum of the instantaneous and delayed elastic response, and $t/(2\eta)$ long-term creep. As above $J(t)$ is the time-dependent compliance and τ is a retardation time. By construction, this expression resembles very much that of the Burger model, with the exception of the kinetics of delayed elasticity. For computational purposes, the Kohlrausch function may be represented by a number of single exponentials (Prony-series) [8b]:

$$\varepsilon = \left[\frac{1}{2G_0} + \frac{t}{2\eta} + \left(\frac{1}{2G_\infty} - \frac{1}{2G_0} \right) \cdot \sum_i v_i \cdot \left(1 - e^{-t/\tau_i} \right) \right] \cdot \sigma_0$$

$$=: J(t) \cdot \sigma_0, \quad \sum_i v_i = 1 \quad (38)$$

For constant strain, the switch to Kohlrausch kinetics yields for the stress:

$$\sigma(t) = 2 \cdot G \cdot \varepsilon_0 \cdot e^{-(t/\tau)^b} =: G(t) \cdot \varepsilon_0 \quad (39)$$

where $G(t)$ is the time-dependent modulus and τ is the a relaxation time. Again, the Kohlrausch-function may be

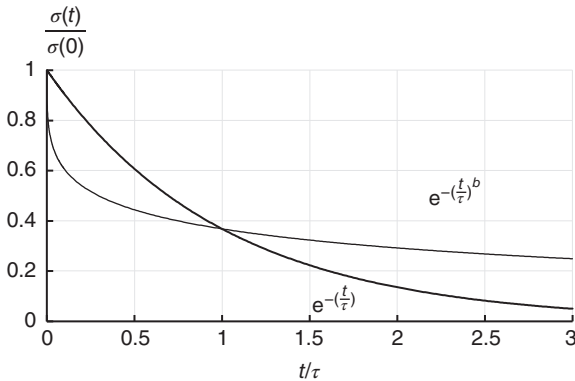


Figure 13 Single exponential function $\exp(-t/\tau)$ versus Kohlrausch (–Williams–Watts) or stretched exponential function $\exp(-(t/\tau)^b)$, $b = 0.3$.

represented by a number of single exponentials (Prony-series):

$$\sigma(t) = 2 \cdot G \cdot \varepsilon_0 \cdot \sum_i v_i \cdot \left(1 - e^{-t/\tau_i} \right) =: G(t) \cdot \varepsilon_0 \quad (40)$$

4.6 Boltzmann's Superposition Principle

In general, i.e. not only for shear, it is assumed that the stress effects arising from strain contributions imposed at different times add up without mutual interference [34d]:

$$\sigma(t) = 2 \cdot G \cdot \sum \Delta \varepsilon_{(\text{at time } t')} e^{-((t-t')/\tau)^b}$$

$$\approx 2 \cdot G \cdot \int_{-\infty}^t e^{-((t-t')/\tau)^b} \cdot \frac{d\varepsilon(t')}{dt'} \cdot dt' \quad (41)$$

4.7 Temperature Dependence of the Relaxation Time

Over the small width of the glass transition range it is legitimate to use an Arrhenius Ansatz for the temperature dependence of the shear viscosity [8c]:

$$\eta = \eta_0 e^{H/R \cdot T} \quad (42)$$

With the assumption of a constant shear modulus, the shear relaxation time of the Maxwell model [8d] then varies in the same way with temperature:

$$\tau = \tau_0 e^{H/R \cdot T} \quad (43)$$

For the present viscoelastic model, one follows this Ansatz for the relaxation or retardation times of Eqs. (37) and (39) by considering not only G_0 and G_∞ but also the b parameter to be constant (thermorheologic simplicity). Further, if one assumes that Eq. (43) can be extended to the nonequilibrium case as done with the corresponding formula (12) for structural relaxation, one obtains [8e]:

$$\tau = \tau_0 \cdot e^{(H/R) \cdot (x/T + (1-x)/T_f)} \quad (44)$$

Even further, if one assumes that both the activation enthalpy H and the nonlinearity parameter x are the same for structural and shear relaxation, the fictive temperature T_f is the same as defined in Eq. (9).

For nonequilibrium calculations with varying temperatures and fictive temperatures, one must convert these expressions into differential equations by calculating time

derivatives of both sides. Preferably, one chooses Prony-series representations as starting points.

4.8 Determination of the Parameters of Shear Viscoelasticity

The parameters may be determined from the phase shift between the force and the elongation during an oscillating load (Figure 14) in mechanical spectroscopy experiments made by dynamic mechanical analysis (DMA) [34e, 35]. The starting point is the time dependence of strain and stress:

$$\varepsilon(t) = \varepsilon_0 \cdot \cos(\omega t), \quad \omega = 2\pi \cdot \nu, \quad \text{or} \quad \varepsilon(t) = \varepsilon_0 \cdot e^{i\omega t} \quad (45)$$

$$\Rightarrow \sigma(t) = 2 \cdot G \cdot i \cdot \omega \cdot \varepsilon_0 \cdot e^{i\omega t} \cdot \int_0^\infty e^{-(t''/\tau)^b} \cdot e^{-i\omega t''} \cdot dt'' \quad (46)$$

With Boltzmann's superposition principle, one obtains for the stress

$$\sigma(t) = \left[2 \cdot G \cdot i \cdot \omega \cdot \int_0^\infty e^{-(t''/\tau)^b} \cdot e^{-i\omega t''} \cdot dt'' \right] \cdot \varepsilon_0 \cdot e^{i\omega t} \quad (47)$$

The term in brackets is called the complex modulus. Introducing the phase shift δ between stress and strain, one obtains:

$$\sigma = \omega \cdot 2 \cdot G_0 \cdot \varepsilon_0 \cdot e^{i\omega t} \cdot e^{i\delta} \quad (48)$$

with

$$\tan(\delta) = \int_0^\infty e^{-(y/\tau)^b} \cdot \cos(\omega y) \cdot dy / \int_0^\infty e^{-(y/\tau)^b} \cdot \sin(\omega y) \cdot dy \quad (49)$$

Owing to the lack of analytic solution, τ and b must in general be determined numerically. Within the glass transition range, however, τ is of the order of 10s so that the following approximation is very good for frequencies higher than 1 Hz [35, 36].

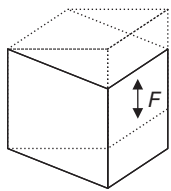


Figure 14 Oscillating shear.

$$\tan(\delta) = \frac{\Gamma(1+b)}{(\omega\tau)^b} \sin\left(\frac{\pi b}{2}\right) + O\left(1/(\omega\tau)^{2b}\right) \quad (50)$$

A higher order analysis leads to:

$$\begin{aligned} \tan(\delta) = & \frac{\Gamma(1+b)}{(\omega\tau)^b} \sin\left(\frac{\pi b}{2}\right) \\ & + \frac{((\Gamma(1+b))^2 - \Gamma(1+2b))}{2(\omega\tau)^{2b}} \sin(\pi b) + O\left(1/(\omega\tau)^{3b}\right) \end{aligned} \quad (51)$$

If $\tan(\delta)$ is known as a function of frequency from DMA, both τ and b may be determined via Eq. (51) with an imprecision of 1 and 2% for $\tan(\delta)$ values lower than 0.17 and 0.24, respectively. If one varies the temperature as well, H can also be obtained. See [35] for the derivation of (50, 51).

An approximate, but simple way to impose shear – either in a static or in a dynamic way – is by bending.

For three-point-bending of thin samples (Figure 15), the elongation s arising from a force F is [37]:

$$s = F \cdot \frac{l^3}{4 \cdot E \cdot d \cdot h^3} \propto \frac{1}{E} \quad (52)$$

With typical values for glass, i.e. $E = 60$ GPa and $\nu = 0.2$ [38], and

$$G = \frac{E}{2(1+\nu)}, \quad K = \frac{E}{3(1-2\nu)}, \quad \frac{1}{E} = \frac{1}{3G} + \frac{1}{9K} \quad (53)$$

one arrives at the fact that about 80% of the elongation is due to shear and only the remaining 20% to compression/dilatation. This ratio may even be increased by a Finite-Element-optimized asymmetric four-point-bending [35, 39, 40] (Figure 16). For $a = 8$ mm, $b = 16$ mm, $c = 6$ mm, $h = 4$ mm, about 86% of the elongation is due to shear.

A typical measurement of this type is carried out by varying both frequency and temperature so that all three parameters τ_0 , b , and H may be determined. (The data set taken for parameter evaluation is limited to data from

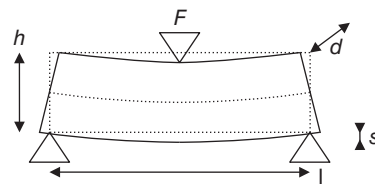


Figure 15 Three-point-bending.

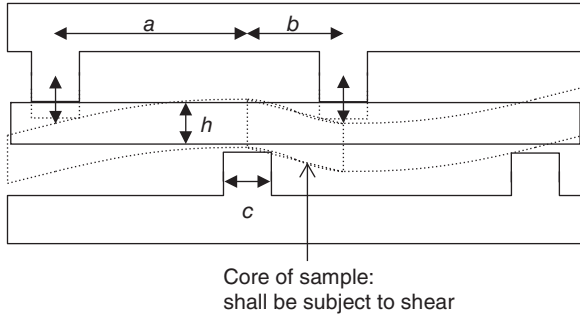


Figure 16 Asymmetric four-point-bending.

above the glass transition range so that equilibrium can be assumed.) Figure 17 shows a DMA on Borofloat33®.

Note that in addition to the dynamic experiments described here, shear relaxation parameters may also be derived from creep measurements, e.g. the ones that have been carried out at Clemson University [41, 42].

5 Bulk Viscoelasticity

Shape-conserving deformation in response to pressure changes is now considered. With respect to shear deformation, the main difference is that the density changes and, consequently, also all other intensive properties.

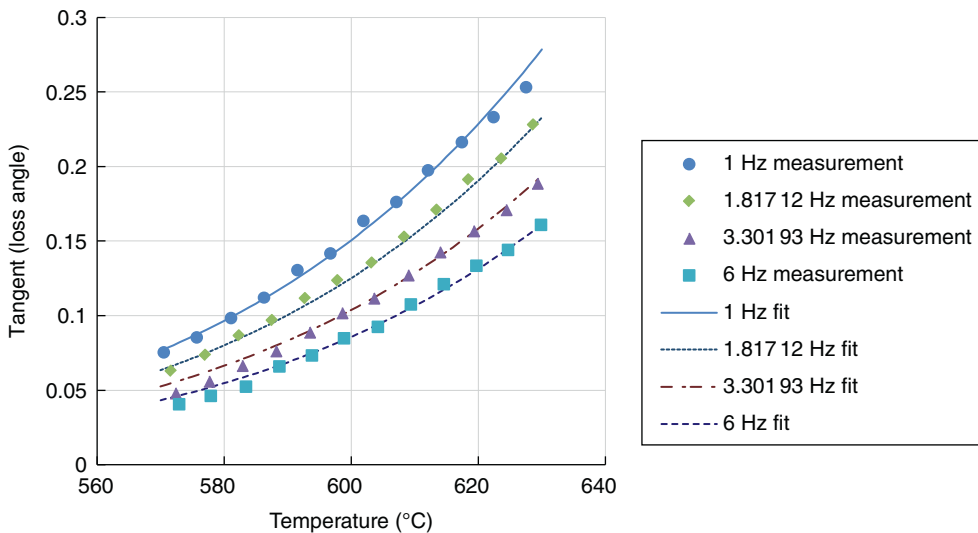


Figure 17 DMA on Borofloat33 in the asymmetric four-point-bending mode ($a = 10$ mm, $b = 12$ mm, $c = 4$ mm, $h = 7$ mm; ratio of shear deformation to total deformation 0.82) leading to $b = 0.323$ 191, $H/R = 52$ 725.8 K, $\tau_0 = 2.256$ 44 · 10⁻²⁶ s. Measurement by GABO EPLEXOR® at the accredited laboratories of SCHOTT AG.

5.1 Bulk Viscoelasticity in Case of Small Pressure Changes

As long as the pressure change is small enough that relaxation properties do not vary significantly, bulk and shear viscoelasticity can be dealt with in a similar way. Consider a glass volume element under pressure (Figure 18). In analogy to (29, 30), but with a Voigt model as starting point, one obtains:

$$F_1 = D \cdot z \rightarrow p_1 = K \cdot 3 \cdot \varepsilon \quad (54)$$

$$F_2 = \eta_V \cdot \frac{A}{d} \cdot \frac{dz}{dt} \rightarrow p_2 = \eta_V \cdot \frac{d\varepsilon}{dt} \quad (55)$$

$$p = p_1 + p_2 \quad (56)$$

The factor 3 allows for the fact that the bulk modulus relates the stress to the strain in three dimensions. η_V is the second or bulk viscosity. Assuming constant pressure p_0 , the strain derived for the Voigt model is [8f]:

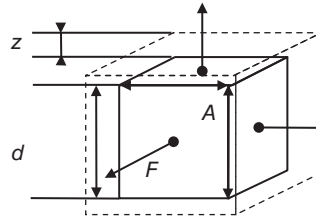


Figure 18 Deformation under pressure.

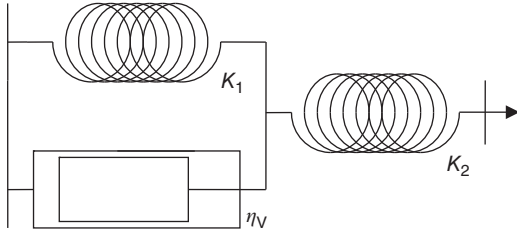


Figure 19 Series of a Voigt model and a spring.

$$\begin{aligned}\varepsilon &= \frac{p_0}{3K} \cdot \left(1 - e^{-t \cdot (3K/\eta_V)}\right) \\ &= \left(\frac{1}{3K} \cdot \left(1 - e^{-t \cdot (3K/\eta_V)}\right)\right) \cdot p_0 = J(t) \cdot p_0\end{aligned}\quad (57)$$

This simple model does not account for all the features observed upon compression of an inorganic glass under pressure. There are two effects, namely instantaneous and delayed strain. In contrast to shear, creep is not possible. Therefore, the simplest model suited is a Voigt model and a spring in series [8g] (Figure 19).

This model allows an illustration of what is observed in glass

- 1) as instantaneous and delayed response to an imposed pressure p_0 :

$$\begin{aligned}\varepsilon &= \left[\left(\frac{1}{3K_2}\right) + \left(\frac{1}{3K_1} \cdot \left(1 - e^{-t \cdot (3K_1/\eta_V)}\right)\right)\right] \cdot p_0 \\ &=: J(t) \cdot p_0\end{aligned}\quad (58)$$

with $J(t)$ being the thus defined compliance;

the first term, i.e. $p_0/(3K_2)$, describes the instantaneous response by the glass, which corresponds to the response of the single spring in the above model; the second term, i.e. $(p_0/(3K_1))(1 - e^{-t(3K_1/\eta_V)})$, describes the delayed response by the glass by creep, which corresponds to the Voigt model above.

- 2) as a partially relaxing response to an imposed strain ε_0 :

$$\begin{aligned}p(t) &= 3 \cdot K_2 \cdot \varepsilon_0 - \frac{3 \cdot K_2 \cdot K_2}{K_1 + K_2} \cdot \varepsilon_0 \cdot \\ &\quad \left(1 - e^{-t \cdot (3 \cdot (K_1 + K_2)/\eta_V)}\right); \end{aligned}\quad (59)$$

the first term, i.e. $3K_2\varepsilon_0$, describes the instantaneous response by the glass, which corresponds to the response of the single spring in the above model; the second term, i.e. $-(3K_2K_2/(K_1 + K_2))\varepsilon_0(1 - e^{-t(3(K_1 + K_2)/\eta_V)})$, describes the diminishment of a part of that response for $t > 0$ and corresponds to the Voigt model above. See [34] or [35] for the mathematical derivation.

Consider the difference between the retardation time $\tau = \eta_V/(3 \cdot K_1)$ and the relaxation time $\tau = \eta_V/(3 \cdot (K_1 + K_2))$.

Again, a better match of theoretical with experimental data is obtained if single exponential functions are replaced with stretched exponential or Kohlrausch(–Williams–Watts)–functions. We also replace K_1, K_2 by the better-suited set K_0, K_∞ (correspondence is obvious).

For constant stress, this gives:

$$\begin{aligned}\varepsilon &= \left[\frac{1}{3K_0} + \frac{1}{3} \left(\frac{1}{K_\infty} - \frac{1}{K_0}\right) \cdot \left(1 - e^{-(t/\tau)^b}\right)\right] \cdot p_0 \\ &=: J(t) \cdot p_0\end{aligned}\quad (60)$$

where $J(t)$ is the time-dependent compliance and τ the retardation time in this case. Again, a Prony series may be advantageous for computational purposes:

$$\begin{aligned}\varepsilon &= \left[\frac{1}{3K_0} + \frac{1}{3} \left(\frac{1}{K_\infty} - \frac{1}{K_0}\right) \cdot \sum_i v_i \cdot \left(1 - e^{-t/\tau_i}\right)\right] \cdot p_0 \\ &=: J(t) \cdot p_0, \quad \sum_i v_i = 1\end{aligned}\quad (61)$$

The expression for constant strain is:

$$\begin{aligned}p(t) &= \left[3 \cdot K_\infty + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot e^{-(t/\tau)^b}\right] \cdot \varepsilon_0 \\ &=: K(t) \cdot \varepsilon_0\end{aligned}\quad (62)$$

where τ is now the relaxation time and $K(t)$ the time-dependent modulus. With a Prony series, this reads:

$$\begin{aligned}p(t) &= \left[3 \cdot K_\infty + (3 \cdot K_0 - 3 \cdot K_\infty) \cdot \sum_i v_i \cdot \left(1 - e^{-t/\tau_i}\right)\right] \cdot \varepsilon_0 \\ &=: K(t) \cdot \varepsilon_0, \quad \sum_i v_i = 1\end{aligned}\quad (63)$$

Concerning the temperature dependence, the assumptions are the same as made above for shear viscoelasticity in that K_0 and K_∞ are considered constant. Likewise, b is considered not to depend on temperature (assumption of thermorheologic simplicity). It is further assumed that the activation enthalpy of bulk relaxation is the same as for shear stress [8h] as well as for structural relaxation and that the same holds for the nonlinearity parameter x so that the relaxation time is given by:

$$\tau = \tau_0 \cdot e^{(H/R) \cdot (x/T + (1-x)/T_f)} \quad (64)$$

where the fictive temperature T_f is the same as defined as in Eq. (9).

For nonequilibrium calculations (varying temperature, varying fictive temperature), one must again convert

these expressions into differential equations by calculating the time derivative of both sides. Once more, one preferably chooses Prony-series representations as starting points.

5.2 Bulk Viscoelasticity for Large Pressure Changes – Fictive Pressure

As described by Eq. (60), the response of a glass to a constant pressure p_0 is both immediate ($p_0/3K_0$) and delayed, with a final value $p_0 \cdot (1/3K_\infty - 1/3K_0)$. The latter can be interpreted as the impact of a second, fictive pressure P_f , with an initially zero value, a final value p_0 , and an intermediate behavior described by unity minus a Kohlrausch function. One then rewrites Eq. (60) as:

$$\varepsilon = \frac{1}{3K_0} \cdot p_0 + \frac{1}{3} \left(\frac{1}{K_\infty} - \frac{1}{K_0} \right) \cdot p_f, \quad (65)$$

$$p_f = p_0 \left(1 - e^{-(t/\tau)^b} \right)$$

Owing to the temperature dependence of the retardation time τ , the fictive pressure is maintained when p_0 is removed after cooling to room temperature. The term $p_f(1/3K_\infty - 1/3K_0)$ may then be used as a measure of permanent densification.

At pressures high enough that the energy pV_m is similar to or higher than RT (V_m , molar volume), the pressure and fictive pressure dependences of the retardation time must also be taken into account. With the TNM(MRS) Ansatz, one obtains for the isothermal case [43]:

$$\tau = \tau_0 \cdot e^{H/RT} \cdot e^{[(p \cdot x' \cdot V^*/RT) + (p_f \cdot (1-x') \cdot V^*/RT)]} \quad (66)$$

i.e. a modified version of the original expression in [43] formulated to ensure that the equilibrium value of τ from the original TNM model follows for $p = 0$. As an analog of the activation enthalpy, V^* is called the activation volume [44] whereas x' is the analog of the nonlinearity parameter x .

6 Perspectives

The linear thermo-viscoelastic theory of relaxation [8, 34], see also as presented here has been extremely successful in applied glass science, see, e.g. [45]. There are shortcomings, however, which demand further research not only from a scientific but also from a glass practitioner's point of view. Three of them shall be shortly discussed here.

The first issue is the essentially non-Arrhenian temperature dependence of relaxation times, which is a characteristic feature of systems with configurational degrees of

freedom and, therefore, one key issue of relaxation theory. The most common explanation has been given by Adam and Gibbs [46]. Originally, it had been developed to explain structural relaxation but has since been generally applied to all relaxation phenomena including the underlying mechanism of viscous flow [47]. Thus, it has been possible to find a theoretical derivation of the widely used empirical (and essentially non-Arrhenian) Vogel–Fulcher–Tamann law of viscosity [48]. The basic assumption of this derivation, however, is that $c_{p,\text{configurational}} = \text{constant}/T$ holds, which is incompatible with the theory presented here. So the applicability of the latter is limited to a small temperature range, e.g. a small temperature range around the glass transition over which a constant value for $c_{p,\text{configurational}}$ and an Arrhenian temperature dependence of the relaxation times can be assumed.

The second issue is the assumption of thermorheologic simplicity that has been challenged by, e.g. Ducroux, Rekhson and Merat [49], who pointed out that thermal shrinkage effects and stress relaxation at temperatures much below the glass transition are poorly predicted by the linear thermo-viscoelastic theory as presented here. Their idea was to replace the constant Kohlrausch parameter b with a temperature-dependent one, i.e. $b(T)$, which takes the value “1” at some temperature between the glass transition and the melting point and decreases with decreasing temperature. Below the glass transition temperature, $b(T)$ will take so low values that the corresponding Kohlrausch function will comprehend comparatively fast relaxation processes, which in return will explain low-temperature relaxation effects. Again, these findings indicate that the applicability of the linear thermo-viscoelastic model as presented here is limited.

The third issue refers to fictive temperature and fictive pressure. An extension of Eq. (66) to the non-isothermal case has to take into account the equivalence of the effects of different parameters. Both a decrease of the fictive temperature and an increase of the fictive pressure lead to a density increase and, in turn, an increase of the relaxation time. This issue is addressed by current research (“density temperature scaling” [50]).

Reviewing the above three points, one comes to the conclusion that there is a definite need, both in glass science and glass industry, for a comprehensive and consistent relaxation model, which allows for all features mentioned.

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3.8

Hyperquenched Glasses: Relaxation and Properties

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1 Introduction

Besides melt-quenching, various different routes may be applied to obtain a glass [1]. For instance, vitreous silica can be prepared via vapor condensation, sol–gel techniques, and argon plasma or heavy-particle bombardment of crystalline silica. The most common route remains melt-quenching, however, which is why much work has been done on melt-quenched glasses to understand the glass transition and relaxation, along with their impact on glass properties (Chapter 3.7). Various experimental and theoretical approaches have been used for this purpose. One of the most effective is hyperquenching-annealing-calorimetric (HAC) scanning whereby a glass-forming liquid is first hyperquenched at a rate higher than 10^5 K/s, subsequently annealed below T_g , and then scanned by differential scanning calorimetry (DSC) [2].

Upon hyperquenching, the liquid structure is arrested in a highly “excited” configurational state owing to the extreme slowing down of the relaxation process with a sudden drop of temperature. Through sudden energetic and structural trapping at high temperatures, a liquid becomes a hyperquenched (HQ) glass far from equilibrium, which has a significantly higher fictive temperature (T_f) than a slowly cooled bulk glass. The energy evolution in the HQ glass during the sub- T_g annealing can be followed and quantified through a DSC upscan. Upon sub- T_g annealing and DSC upscanning, the highly excited configurational state is gradually relaxing so that T_f decreases. This feature makes it possible to observe the energetic development of a HQ glass well below T_g from

which information is gained about the structural heterogeneity of the corresponding liquid at $T = T_f$. From enthalpy relaxation, one can then infer how the potential energy and structure of the glass evolve upon annealing or dynamic heating and how both depend on the chemical composition of the material. In addition, the atomic vibrational dynamics in HQ glasses upon annealing can be observed with neutron, inelastic X-ray, or nuclear inelastic scattering techniques.

The present chapter reviews advances made in understanding relaxation of HQ glasses. The methods for determining T_f and cooling rate are presented. The relaxation features are correlated with the energetic and structural heterogeneities in glass. Striking differences in relaxation modes between strong and fragile HQ glasses are shown and discussed. As an effective method, the HAC approach is used to identify the so-called Johari–Goldstein relaxation and to reveal the thermodynamic change accompanied by the fragile-to-strong liquid transition. The potential-energy dependence of the vibrational properties of HQ glasses is illustrated. Finally, some perspectives in this research are briefly described.

2 Fictive Temperature and Cooling Rates

The fictive temperature (T_f) of a glass is the temperature at which the structure of its equilibrium liquid has been frozen-in (Chapter 3.7, [3–5]). It is determined by the cooling rate and the pressure applied to the liquid and represents the average level of the glass on the potential energy landscape. One of the reasons why it is important to quantify the thermal history of the glass in terms of both T_f and the cooling rate of glass is that these parameters exert a strong impact on mechanical and optical properties so that they are crucial for glass production

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process. The problem is indeed of great practical interest because it concerns in particular mineral and stone wool, which are very rapidly drawn and cooled down as fibers (Chapter 9.3), as well as metallic glasses produced as ribbons (Chapter 7.10).

In preamble, it must be stressed that the relaxation and physical properties substantially differ for HQ and slowly cooled glasses of the same chemical composition [6–8]. To picture the basics of enthalpy relaxation in HQ glasses, a stone-wool sample will be selected here. As produced with a cascade process (Chapter 9.3) and hyperquenching at a disc rotation speed of about 6000 rpm [2], the fibers have a mean diameter of about 3.5 μm and a standard T_g of 944 K (Figure 1). Their composition is (wt %) 41.5 SiO_2 , 21.3 Al_2O_3 , 1.6 TiO_2 , 7.3 Fe_2O_3 , 13.9 CaO , 11.7 MgO , 1.6 Na_2O , and 0.8 K_2O . In DSC upscans (Figure 1), there is a large difference between the measurements performed on the HQ sample (C_{p1}) and on the same sample reheated after cooling at 10 K/min (C_{p2}), which will be termed the *standard* glass sample [5]. In other words, the excess C_p of the HQ with respect to the standard glass originates in a potential energy gradually recovers upon dynamic heating, which of course depends on both glass composition and fictive temperature. Since the mechanical work done upon fiber stretching is small enough to be neglected, the excess enthalpy can itself be assumed to be the excess internal energy stored during hyperquenching.

To proceed further, it is useful to define T_c as the onset temperature ($=0.52 T_g$) of the enthalpy release, above which the fictive temperature gradually drops with increasing temperatures; T_e as the equilibrium temperature ($=1.06 T_g$) at which the quenched-in energy is completely released; T_s as the *shoulder* temperature ($=0.72 T_g$)

at which $C_{p1} = C_{p2}$ and the liquid returns to internal equilibrium; and T_{eq} as any temperature above the glass transition range [5]. The enthalpy (ΔH) released upon heating is then given by:

$$\Delta H = \int_{T_c}^{T_{eq}} (C_{p2} - C_{p1}) dT. \quad (1)$$

This excess enthalpy can alternatively be characterized by the fictive temperature T_f of the HQ glass. This parameter is determined with the enthalpy-matching method [5], which assumes that ΔH represents the excess enthalpy of the liquid with respect to the glass over the interval $T_g - T_f$ (Figure 2):

$$\int_{T_c}^{T_{eq}} (C_{p2} - C_{p1}) dT = \int_{T_{g,ref}}^{T_f} (C_{pl} - C_{pg}) dT, \quad (2)$$

where C_{pl} and C_{pg} are the isobaric liquid and glass heat capacities, respectively. For the HQ stone wool, one finds in this way a T_f of 1155 K ($=1.23 T_g$) if the C_{pg} curve is extrapolated to the liquid region with an equation of the form

$$C_{pg} = a + bT + c/T^2 + d/T^{0.5}, \quad (3)$$

where a , b , c , and d are constants.

If the viscosity–temperature relationship of the glass-forming liquid is known, one can in addition calculate the cooling rate q_c of the HQ glass with [5]:

$$\log q_c = 11.35 - \log \eta(T_f). \quad (4)$$

In Eq. (4), $\eta(T_f)$ is the viscosity at temperature T_f , which is 5.05 Pa.s, so that the cooling rate of the stone-wool fibers is about 2×10^6 K/s.

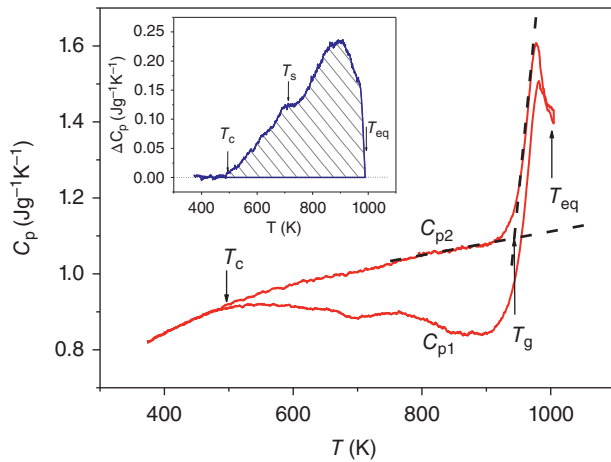


Figure 1 Excess enthalpy of a stone wool as given by the difference between the DSC of the HQ (C_{p1}) and standard (C_{p2}) samples at the same rate of 10 K/min. Inset: excess capacity, $\Delta C_p = C_{p2} - C_{p1}$, as a function of temperature (characteristic temperatures defined in text).

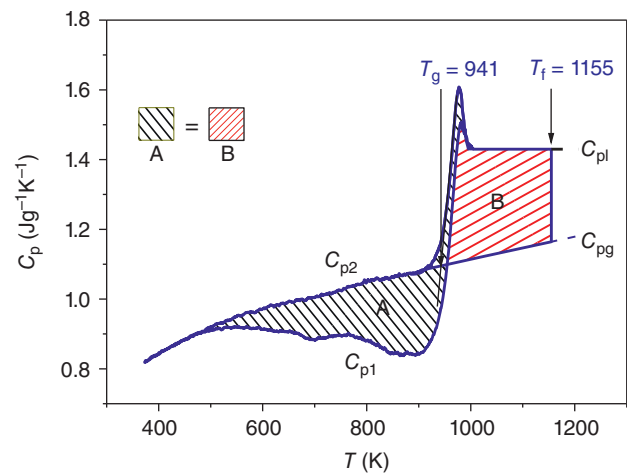


Figure 2 Determination of the fictive temperature T_f of the HQ stone wool with the energy-matching method. Same C_p data as in Figure 1, C_{pl} and C_{pg} being the liquid and glass heat capacities, respectively, and T_g the standard glass transition temperature.

3 Sub- T_g Relaxation

Determinations of excess enthalpies are just a first step in the characterization of HQ glasses as it is also important to know how enthalpy relaxes, i.e. to evaluate the rates at which the fictive temperature change and the excess enthalpy is released upon either static annealing or dynamic heating. Although enthalpy relaxation is a non-linear, non-exponential process, it has been extensively studied owing to its importance for understanding the nature of glass and the glass transition and for optimizing physical properties of glass products [4]. Most studies have dealt with slowly cooled glasses but scientists have recently realized that the enhanced nonequilibrium features of HQ glass fibers and ribbons make these materials particularly interesting for studying the glass transition and relaxation phenomena [2]. This is why sub- T_g annealing is a key approach to obtain dynamic and thermodynamic information on the glass transition.

Two parameters are independently acted upon in this respect, namely, the annealing temperature for a given time and the annealing time at a given temperature. Taking as a DSC reference the standard stone wool, one observes in the first case that, for HQ samples cooled at a rate of 2×10^6 K/s [2], the left cutoff of the enthalpy release peak (i.e. the exotherm below T_g) gradually shifts to higher temperatures until the peak completely disappears when the temperature T_a of eight-day annealing increases (Figure 3). Upon annealing, the configurational states of higher potential energy (or weaker bonding) are transformed into states of lower potential energy. When T_a is sufficiently high (but still lower than T_g), a pre-endotherm occurs below the onset temperature of the

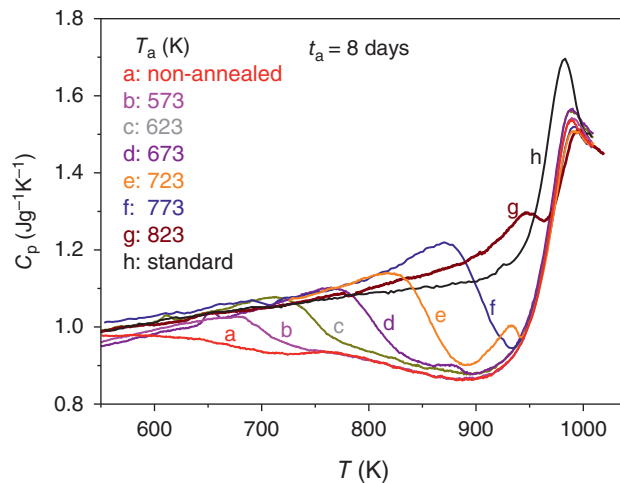


Figure 3 Effect of the annealing temperature (T_a) on the enthalpy relaxation of stone-wool fibers annealed for eight days. Thick, dark curve: DSC upscan curve of the standard sample. Up- and downscan rates of 20 K/min.

exotherm (Figure 3). This pre-endotherm becomes larger with increasing T_a , but its onset remains constant. At the same time, the exotherm becomes smaller with T_a so that the exotherm and endotherm coexist in a certain range of T_a .

The annealing time t_a has a similar effect on the calorimetric response of the HQ stone wool at $T_a = 723$ K (Figure 4). When the annealed sample is heated from room temperature to T_e , a pre-endotherm again appears, followed by an exotherm [2]. The pre-endotherm becomes more pronounced with t_a and shifts to higher temperatures until the exotherm disappears. This feature implies that, upon sufficient annealing, the potential energy of weakly bonded structural units in the HQ glass drops to a level below that of the standard glass, and finally to that corresponding to the given T_a , whereas that of strongly bonded structural species remains higher than that of the standard glass.

Besides, a simple way to determine the relaxation kinetics is to consider the time dependence of the fraction $\Delta H_{\text{rem}}/\Delta H_{\text{tot}}$ of the excess enthalpy that has not been released during the DSC upscan (Figure 4, inset). One can then make a fit made to the experimental data with a Kohlrausch function $\Delta H_{\text{rem}}/\Delta H_{\text{tot}} = \exp[-(t/\tau)^\beta]$, where τ is the characteristic, temperature-dependent relaxation time, and $\beta \in (0, 1)$ is the stretching exponent describing the broadness of the relaxation time distribution (Chapter 3.7). The value $\beta = 0.16$ obtained for $T_a/T_g = 0.66$ is much lower than that those found in the energy-landscape influenced regime ($0.45 < T/T_g < 1$). The small

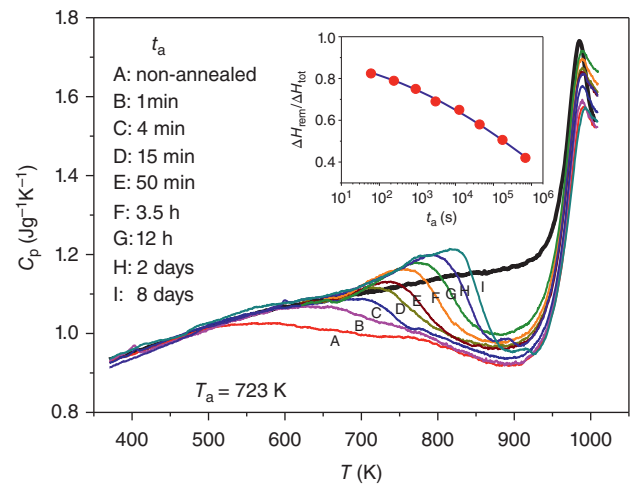


Figure 4 Effect of the annealing time (t_a) on the enthalpy relaxation of stone-wool fibers annealed at 723 K. Thick, dark curve: DSC upscan curve of the standard sample; up- and downscan rates of 20 K/min. Inset: $\Delta H_{\text{rem}}/\Delta H_{\text{tot}}$ as a function of t_a , where ΔH_{rem} is the enthalpy remaining in the sample after annealing and ΔH_{tot} is the total energy stored by HQ; solid line: Kohlrausch fit to the experimental data.

β value derived thus indicates that the distribution of relaxation times of the HQ glass upon annealing at 723 K becomes broader compared to that of the standard glass.

Additional information on energetic and structural heterogeneities in glass near T_g may be obtained through stepwise annealing studies [2]. Upon annealing, the relaxing parts of microstructures become less disordered and more stable in comparison with those of the standard glass. When the annealed HQ glass is upscanned in DSC, the degree of disorder in the relaxing part of the structure increases and gradually approaches that of the standard sample. This process leads to an endothermic event, i.e. to a pre-endotherm whose extent increases with both T_a and t_a . The pre-endotherm occurs only when the glass is hyperquenched and then annealed. It is more pronounced for glasses with higher T_f than for those with lower T_f under the same annealing conditions [2, 6].

Additional features of the pre-endotherm of the annealed stone-wool samples are noteworthy (Figure 5). The sample annealed for eight days at 773 K exhibits a pronounced pre-endotherm (Curve 1 of Figure 5), which completely disappears when the annealed sample is reheated in DSC to the crossover temperature ($T_{\text{cross}} = 897$ K), then cooled down to room temperature, and finally reheated to the maximum temperature (Curve 2 of Figure 5). At the same time, the exotherm remains unaffected.

The pre-endotherm of the annealed HQ glass and the T_g endotherm of the standard sample have different physical origins. One can eliminate the former and then

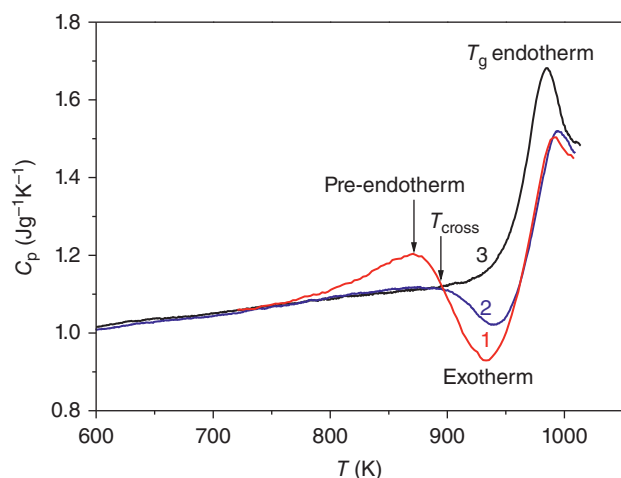


Figure 5 Isobaric heat capacity (C_p) as a function of temperature (T) showing the influence of heating condition on the pre-endotherm of the stone-wool sample subjected to a sufficient degree of the annealing. Curve 1: the sample annealed at 773 K for eight days; Curve 2: the sample annealed at 773 K for eight days, and then heated from 298 K to the crossover temperature (T_{cross}) of 897 K; Curve 3: the standard sample.

recover it by properly choosing heating and reannealing procedures. In contrast, the T_g endotherm is not removable by heating and annealing processes as it always occurs in up- and downscan as long as crystallization is avoided. The T_g endotherm is of course caused by the glass transition, which is accompanied by an abrupt increase in configurational entropy whereas the pre-endotherm is a signature of the strong non-exponential relaxation of the HQ glass upon annealing. As a matter of fact, all types of glasses have a spectrum of relaxation times, which implies the existence of many micro domains of different T_g values [2].

4 Anomalous Relaxation

The stone wool considered in previous sections is a relatively fragile liquid, whose viscosity–temperature relation is thus strongly non-Arrhenian (Chapter 4.1). Since relaxation is closely related to liquid fragility (Chapter 3.7), it is useful to turn now to germania (GeO_2), a strong liquid [9] whose HQ glass will be compared with that of calcium metaphosphate (CaP_2O_6), another fragile melt [10]. Even when plotting the DSC ΔC_p curves against the normalized temperatures T/T_g to account for T_g differences, there is a striking difference between both materials in terms of the T_a dependence of enthalpy relaxation. For HQ CaP_2O_6 (Figure 6a), the left cutoff of the ΔC_p peak gradually shifts to higher temperature with increasing T_a ($< T_g$) for $t_a = 12$ hours, whereas the right cutoff remains unmoved until the entire ΔC_p peak disappears. In contrast, for HQ GeO_2 (Figure 6b), the entire ΔC_p peak height becomes lower with increasing T_a ($< T_g$) for $t_a = 24$ hours. In other words, enthalpy release much differs in strong and fragile systems regarding the effects of the annealing temperature.

For HQ GeO_2 , annealing at a single temperature T_a below T_g (representing kinetic energy) can thus make complete relaxation of all structural units possible. In other words, the release of potential energy affects all network structural units and, hence, all sub-fictive temperatures (sub- T_f) characterizing distinct microstates with a kinetics that is determined by both T_a and t_a . Such a type of relaxation confirms that there exists only a single megabasin in the energy landscape of a strong system [11]. Similar relaxation phenomena are observed for HQ SiO_2 glass [11], indicating that the simultaneous and collective relaxation of all structural units is a universal feature for strong glass formers. In contrast (Figure 6a), relaxation in fragile systems proceeds in such a manner that some configurational states relax whereas others still remain unaffected, pointing to a great many well-separated megabasins in the potential energy landscape [11].

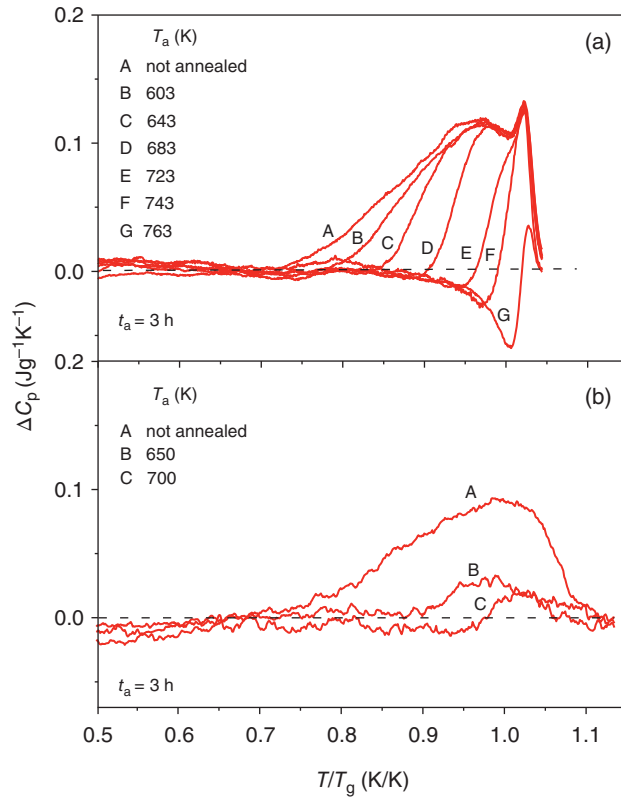


Figure 6 Effect of the annealing temperature (T_a) on the ΔC_p curves. (a) HQ CaP_2O_6 (fragile system) annealed at different T_a for the annealing time of $t_a = 3$ h; (b) HQ GeO_2 (strong system) annealed at different T_a for $t_a = 3$ hours. The DSC up- and downscan rates are 0.33 K/s. The T_g values of CaP_2O_6 and GeO_2 are 797 and 830 K, respectively. Dashed line: the standard sample.

Another pronounced difference in enthalpy relaxation between the fragile and strong systems is revealed by Figure 6a. In annealed HQ CaP_2O_6 , a pre-endotherm is observed before the exothermic peak occurs when T_a is sufficiently high but below T_g . Such a pre-endotherm is not observed for HQ GeO_2 , which is further evidence for less energetic and structural heterogeneities in strong systems compared with fragile ones. Because the effects of t_a and T_a on the enthalpy relaxation of both HQ CaP_2O_6 and GeO_2 are similar (Figure 7), the influence of t_a on the potential-energy landscape of the strong systems differs from that of fragile ones. These findings are not only of scientific interest, but also of potential technological importance. The optical and mechanical properties of glass fibers are strongly influenced by sub- T_g annealing. An improved knowledge of relaxation of HQ glasses may thus contribute to optimizing the forming and annealing processes of $\text{GeO}_2/\text{SiO}_2$ fibers with respect to these properties.

In the same spirit, many systems have been studied by means of the HAC approach to explore the effect of the

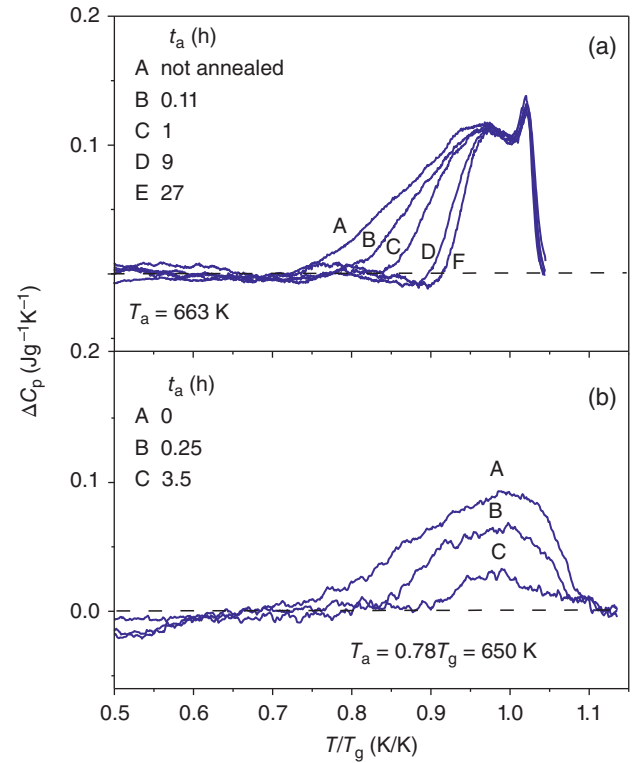


Figure 7 Effect of the annealing time t_a on the ΔC_p curve. (a) HQ CaP_2O_6 (fragile system) annealed at $T_a = 663$ K for different t_a ; (b) HQ GeO_2 (strong system) annealed at $T_a = 650$ K for different t_a . The DSC up- and downscan rates are 0.33 K/s. Dashed line: $\Delta C_p = 0$ for the standard sample.

liquid fragility on enthalpy relaxation in HQ glasses. It has been found that two main distributions of relaxation times determine the shape of the excess ΔC_p curves of the annealed HQ glasses. As reflected by high- T relaxation around T_g , one is associated with α relaxation, which accounts for global relaxation of the structural network. As embodied by relaxation well below T_g , the other is associated with β relaxation, which is likely related to local potential-energy lowering between network modifiers and non-bridging oxygens.

5 Modeling of Sub- T_g Relaxation

In glass relaxation studies, the Tool–Narayanaswamy–Moynihan (TNM) model (Chapter 3.7, [12]) is widely used since it describes reasonably well the calorimetric response to annealing temperature and time. Alone, however, it does not describe enthalpy relaxation in HQ glasses [13] or upon sub- T_g annealing. In this context, therefore, another promising approach is based on a new stretching function in the TNM model, which describes two well-separated distributions of relaxation

times and takes into account the substantial broadening of the glass transition region during the HQ process [14]. For fragile systems, this modified model predicts well the enthalpy response of both HQ and partially annealed HQ glasses under dynamic and isothermal heating although its physical foundations remain to be built firmly. In this respect, one should mention that a molecular dynamic simulation study has also succeeded in reproducing the annealing-induced pre-endotherm in HQ glassy water [13]. But there are still no suitable models for describing sub- T_g relaxation in strong glass formers such as HQ GeO_2 and SiO_2 . This is a challenging subject for future research.

6 Boson Peak

The vibrational dynamics exerts a determining influence on physical properties in both the solid and liquid states (Chapter 3.4). In this respect, an intriguing feature of the vibrational density of states $g(E)$ of amorphous substances is the existence of an excess of low-frequency states relative to the $g(E)/E^2$ values predicted by Debye theory. This excess manifests itself in incoherent inelastic neutron scattering or Raman spectra as the *boson peak*, between 2 and 10 meV, whose intensity depends on temperature, pressure, and chemical composition (Chapter 3.4, [6]). Although this energy interval clearly indicates that the peak is related to intermediate-range order, its structural origin remains debated in part because slowly cooled glasses have mostly been investigated. It is nonetheless agreed that distinct configurational excitations involve structures in which low-frequency modes, presumably with a transverse character, are generated.

Since they possess much higher potential energies and larger degrees of disorder, HQ glasses represent good systems to clarify the origin of the boson peak in terms of low-frequency modes involving large clusters, nanoparticles, mismatching or connected rings, or small tetrahedral rocking groups. In addition, HQ glasses have over liquids the advantage of sampling high-temperature structures that can be studied without any adverse effects from quasielastic scattering [6]. For this purpose, cold-neutron inelastic scattering with time-of-flight measurements is a particularly appropriate technique because its output, $Z(\omega)$, approximates the vibrational density of states if effects such as multiphonon and multiple scattering can be ignored.

Such experiments made for stone-wool fibers clearly show how the intensity of the boson peak decreases with decreasing T_f from HQ to superannealed glass before vanishing in the crystallized material [6]. The vibrational properties of a HQ and a well-annealed glass have been

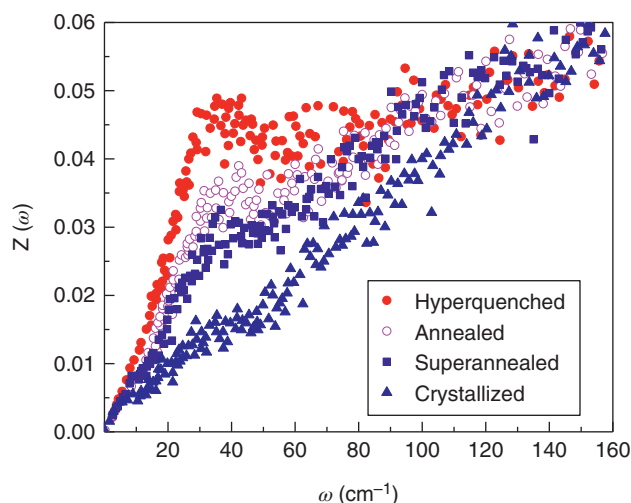


Figure 8 Influence of structural disorder on the $Z(\omega)$ function regarded as an approximate representation of the vibrational density of states. Data shown up to 160 cm^{-1} for the stone wool in hyperquenched, standard-cooled, annealed, and crystalline states, respectively [6]. Annealed glass obtained by annealing of the HQ sample for 21 hours at 894 K ($0.94T_g$), crystallized sample by holding the glass at 1156 K for 150 minutes.

studied by nuclear inelastic scattering [15]. Although the former shows a higher number of vibrational states in the low-energy region than the latter, both vibrational densities of state become identical if they are renormalized after rescaling the energy axes in Debye energy units. This result indicates, on the one hand, that the decrease of Debye energy originates in density and sound velocity decreases and, on the other hand, that the effects of quenching and annealing on the boson peak may be described in terms of the transformation of a continuous medium. In particular, quenching does not affect the intensity of the boson peak, i.e. the relative excess of states above the Debye level so that the increase of the number of states is compensated by a corresponding increase of the Debye level. The higher heat capacity of glasses than crystals is not due to disorder, but to a lower density [16]. It is likely, therefore, that suppression of the boson peak upon more complete annealing (Figure 8) might simply be caused by an increase of the sample density.

7 Resolving Glass Problems Via Hyperquenching-Annealing Calorimetry

7.1 Johari–Goldstein (JG) Relaxation

Among different kinds of secondary (β) relaxations preceding the primary (α) process, a slow one was discovered on rigid molecules by Johari and Goldstein in 1970 [17].

This Johari–Goldstein (JG) relaxation plays an important role in the glass transition because it involves motion of all parts of a molecule. Even though much progress has been made in its study, the physical nature of this motion is still far from thoroughly understood. To the important question of whether the JG relaxation also occurs in strong glasses and in metallic glasses, one can answer by applying the HAC approach.

With this approach, it has been found that the strong HQ GeO_2 relaxes in such a manner that all secondary relaxation units contribute to the primary relaxation [11]. By analyzing the dynamic properties of the secondary (β) relaxation in the HQ GeO_2 glass, one identifies two typical features of JG relaxation. First, the quantitative relationship observed here between E_β , the activation energy of β relaxation, and T_g , $E_\beta = 23.5RT_g$, agrees well with the empirical expression of the JG relaxation, i.e. $E_\beta = 24 RT_g$ [18]. Second, the characteristic β relaxation time of GeO_2 glass at T_g is about 10 seconds, which is longer than that of relatively fragile systems. These results confirm that the JG peak in strong glasses is hidden in the α peak of the dielectric-loss curves. With the HAC approach, the dynamics of β relaxation in HQ metallic glasses like $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ ribbons in addition exhibits a typical feature of the genuine JG relaxation, since the variation of its activation energy (E_β) with T_g , namely, $E_\beta = 26.8 RT_g$, is also close to the aforementioned relation. In summary, JG relaxations are intrinsic features of both strong glass formers and metallic glass formers.

7.2 Mechanical Properties

In centrifugal fiber spinning, glasses are not only thermally hyperquenched, but also mechanically stretched with a degree of anisotropy that is frozen-in upon quenching and can be enhanced through increases of the axial stretching force. The anisotropy also depends on composition and, thus, on structure through the relative easiness with which the structural units align themselves with the fiber direction. As quantified by optical birefringence measurements, a higher anisotropy can thus be achieved with the same stretching force for glasses with one-dimensional (e.g. metaphosphate) than with three-dimensional (e.g. soda-lime-silicate) structural units. Enthalpy relaxation upon annealing or dynamic heating includes such a contribution from structural anisotropy. Compared with the slow mechanisms discussed above for the whole glass network, the difference is that anisotropy relaxation is fast because it involves only a more random arrangement of the local structure.

Regarding mechanical properties, the important point is that anisotropy relaxation causes the tensile strength of glass fibers to decrease, in agreement with the fact that fiber strength increases with the axial force applied [8]. In

other words, a larger drawing force yields thinner fibers, a higher quenching rate, and, hence, a higher T_f . In turn, a higher T_f is associated with a higher optical birefringence. Another noteworthy feature is that an increase of T_f has a negative impact on both the hardness (H) and elastic modulus (E) of glass fibers [7] as observed when these properties are successfully measured from indentation experiments made on single, thin glass fibers. The dependence of such mechanical properties on T_f can be studied for a wide range of HQ rates. Both H and E decrease linearly with a decrease of the fiber diameter (5–20 μm), i.e. with an increase of T_f . This trend may be readily understood in terms of an increase of the free volume with increasing T_f , which results in a lower resistance to indentation and deformation [7]. By varying the HQ rate and the degree of the sub- T_g annealing, one can in fact tune not only the mechanical, but also the optical properties of the glass.

7.3 Fragile-to-Strong Transitions

The fragility of a liquid represents the extent to which the temperature dependence of its viscosity and relaxation times depart from Arrhenian variations. The concept has in particular been widely used to characterize the dynamic properties of liquids in the vicinity of T_g . Based on this concept, liquids are normally classified as fragile and strong liquids (Chapter 4.1). An interesting observation made in this respect is that some glass-forming liquids do not conform to the conventional “strong/fragile” scheme, however, because their transport properties such as viscosity, self-diffusion constant, and relaxation time exhibit fragile-to-strong (F–S) transitions upon cooling [19]. Specifically, the viscosity of these liquids strongly deviates from Arrhenian laws around the liquidus (T_{liq}), but is close to Arrhenian near the glass transition range. These F–S transitions are a general feature of metallic glass-forming liquids so that an important question is to determine their structural origin. It is a challenge to answer it, however, because of very rapid incipient crystallization in the temperature and viscosity ranges where the transition takes place.

In spite of these difficulties, valuable information has been indirectly derived from HAC experiments. As illustrated by HQ $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ glass ribbons (Figure 9), a striking anomalous relaxation phenomenon is observed in the form of three-stage sub- T_g relaxation when T_a increases from 583 to 623 K, i.e. in the temperature range of the F–S transition. Likewise, changes in the two low- Q pre-peaks (P_1 and P_2) but not in the main peak (P_m) of the structure factor $S(Q)$ are observed with increasing T_a in X-ray scattering experiments (Figure 10). This constant P_m position indicates that the structural units that define short-range order (SRO) are stable. In contrast, the P_2

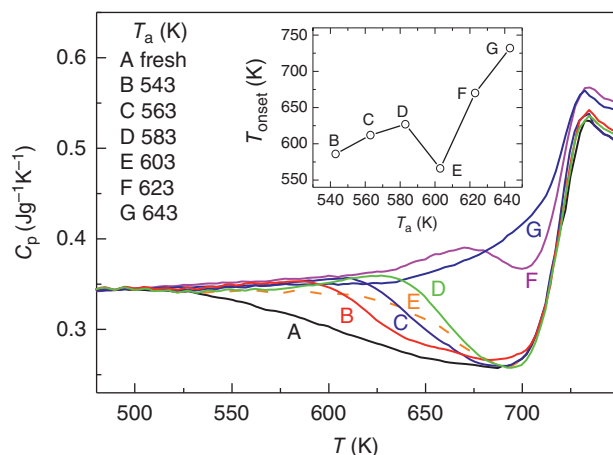


Figure 9 Effect of the temperature (T_a) of one-hour annealing on enthalpy relaxation as seen from the isobaric heat capacity (C_p) of HQ Cu₄₆Zr₄₆Al₈ glass ribbons [19]. Inset: relationship between T_a and the onset temperature of the exothermic peak (T_{onset}).

position slightly shifts toward higher Q values with increasing T_a , which could point to a monotonic decrease of intermediate-range ordering units. As for the position of P_1 , it varies in a zig-zag manner upon T_a increases, first shifting to lower Q values below 583 K, then to higher values from 593 to 613 K, and again to lower values above 623 K. Interestingly, this non-monotonic evolution is observed in the same T_a interval as that of the three-stage enthalpy relaxation (Figure 9, inset), which thus implies that the F–S transition of CuZrAl liquid is caused by a drastic transition in its medium-range order (MRO).

To go one step further, one can calculate the size of the structural unit involved in the process from Ehrenfest's formula $\ln \Omega_g = (h_m - h_c)/RT_g$, where Q_{pp} is the position of the P_1 pre-peak, and can thus determine its dependence upon T_a (Figure 10, inset). As expected, a marked negative anomaly is found between 600 and 620 K. It indicates a discontinuous evolution in MRO at the F–S transition, which cannot be accounted for by Adam–Gibbs theory of relaxation processes in which the size of cooperatively rearranging regions in the liquid is assumed to be a smooth function of temperature. Instead, the R_c decrease coinciding with the anomalous in enthalpy of the supercooled CuZr(Al) liquid upon cooling at around $1.3\text{--}1.4T_g$ has been attributed to dissociation of structural units into smaller clusters. Phenomenologically, the F–S transition would thus result from competition among MRO clusters composed of different locally ordered configurations [19].

7.4 Detection of Structural Heterogeneity in Glass

Structural and dynamic heterogeneities are universal in glass and are intimately connected to the glass transition relaxation phenomena. Dynamic heterogeneities in supercooled liquids, for instance, imply the existence of significant fluctuations upon quenching as a result of the reduction in the number of independent regions. Direct evidence for dynamic heterogeneities has been obtained from both calorimetric analysis and modeling of glass relaxation during sub- T_g annealing. Since

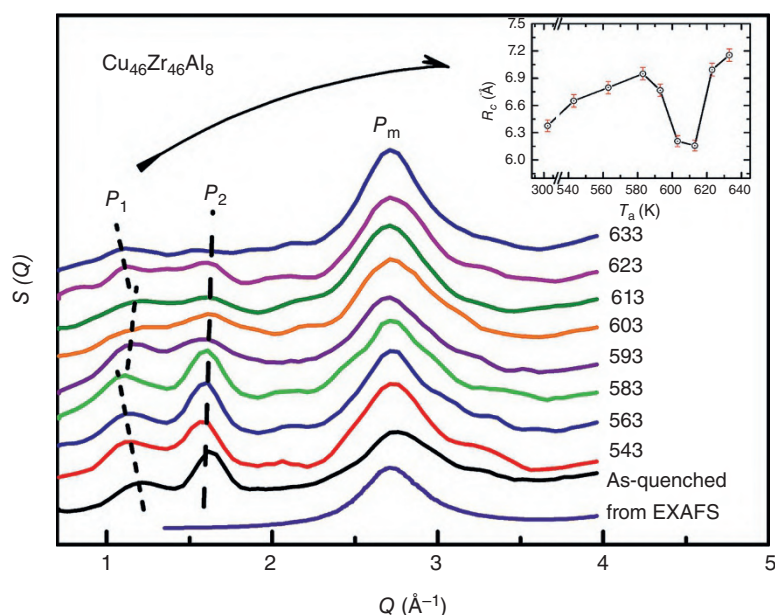


Figure 10 Non-monotonic evolution of the structure factor $S(Q)$ of HQ Cu₄₆Zr₄₆Al₈ glass ribbons with increasing annealing temperature (T_a) below T_g for one hour [19]. Bottom curve extracted from extended X-ray absorption fine structure (EXAFS) data. Shifts of the two pre-peaks indicated by dashed lines. Inset: structural unit size R_c of the first pre-peak (P_1) as a function of T_a .

dynamic heterogeneities are considered to have a structural origin, much effort has been made to clarify their mutual relationships.

In addition to structural properties, the potential energy in glass correlates with the dynamics at certain length scale since the mobility of an entity is higher when its potential energy is lower. Studies of enthalpy relaxation in HQ glasses have provided information on the energetic and structural heterogeneities in the supercooled liquids. With the HAC approach, it has, for instance, been established that the stepwise pattern of enthalpy release from HQ glasses with increasing T_a is due to structural heterogeneities [2]. The calorimetric signature of the structural heterogeneity has been obtained in HQ glass-wool fibers with the 20.8 CaO·15.6 MgO·62.2 SiO₂ composition (in wt %), hereafter abbreviated as HQ-CMS glass [20]. The fiber sample was attenuated from its parent melt at about 1873 K by means of a centrifugal cascade process. During the process, the fibers were hyperquenched at about 2×10^6 K/s. The HQ-CMS glass was subjected to a sub- T_g annealing protocol. The DSC results exhibit a striking phenomenon: two separated sub- T_g relaxation peaks in the HQ-CMS glass, implying the existence of two distinct structural domains of higher and lower potential energies, respectively. At the nano-scale, the higher energy domains are so unstable that they order even upon hyperquenching. This conclusion is verified by high-resolution transmission-electron microscopy images exhibiting nano-ordered domains in the glass matrix. The higher energy domains relax like a strong glass phase, whereas the lower energy domains do it like a fragile one.

8 Perspectives

The HAC approach is a sensitive and useful tool for studying the dynamics and thermodynamics of glasses and supercooled liquids that should benefit from technological and computing advances. Whereas new quenching technologies should make quenching rates faster than the current 10^{6-7} K/s possible, improved computing means should in contrast allow simulations to be made at rates slower than the current quenching rates (Chapter 2.9). A first promising outcome of such advances would be the possibility to probe the structure, potential energy, and dynamics of a liquid in the crystallization region of poorly vitrifiable systems, especially those showing fragile-to-strong transitions. A second positive outcome would be more extensive confrontations between experimental results and theoretical prediction of glass structure and dynamics. With the additional help of advanced microscopic characterization

techniques, these two aspects should allow structural heterogeneities in glasses to be explored quantitatively. In turn, key problems in glass sciences should be better addressed and receive new solutions. Cases in point are polyamorphic, liquid-liquid and fragile-to-strong liquid transitions, glass-formation, and structure-property relationships. Both applied glass science and technology are expected to be considerably advanced in this way.

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3.9

Polyamorphism and Liquid–Liquid Phase Transitions

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1 Introduction

Crystalline materials undergo first- and second-order phase transitions, leading to polymorphs having different structures and distinct physical properties. Similarly, different amorphous forms of glasses and other structurally disordered amorphous substances have been produced, depending on conditions of formation and processing. Polyamorphic transformations between different amorphous “phases” that appear to mimic crystalline phase transitions also occur as a function of variables such as pressure (P) or temperature (T). Because glasses and other amorphous materials are not in internal thermodynamic equilibrium, such analogies must be made with care, however. Thermodynamic transitions between non-crystalline phases can and do occur within the stable or supercooled liquid state, and these can be extrapolated below the glass transformation range in order to understand polyamorphic effects. Here we describe the topics of polyamorphism and density- or entropy-driven liquid–liquid phase transitions (LLPT) with examples drawn from systems that exhibit different phenomenological aspects. We begin with a discussion of LLPT that can occur as a function of pressure or temperature between liquid phases of the same substance that have distinct structures and thermodynamic properties.

Acronyms

CEL configurational energy landscape
HDA high-density amorphous (solid)

HDL high-density liquid
LLPT liquid–liquid phase transition
LDA low-density amorphous (solid)
LDL low-density liquid
PIA pressure-induced amorphization

2 Liquid–Liquid Phase Transitions and Polyamorphism

2.1 Density- and Entropy-Driven Phase Transitions in Solids

Thermodynamic transitions between crystalline phases are typically described according to Ehrenfest’s classification as of first or second order. In a first-order transition, two phases A and B have different free energies, $G(P, T)$, except at the equilibrium transition point (T_{tr}, P_{tr}) in temperature or pressure space where $G_A = G_B$, but discontinuities occur between the enthalpy (H), entropy (S), and volume (V) parameters of both phases. The $G(P, T)$ curves of both phases can be extended metastably into the pressure or temperature stability domain of the other, so a hysteresis results along with metastable coexistence of the two polymorphs. This is the type of transition envisaged in most discussions of polyamorphism and LLPT. The phenomena can also appear in relation to other pairs of coupled intensive/extensive thermodynamic variables. In a second-order transition, there is only a single common $G(P, T)$ relation for both phases that exhibits a break in slope at the transition point. Such second-order transformations have been suggested to interpret polyamorphism occurring in certain glasses and liquids, but the arguments are best considered after the concept of first-order LLPT has been introduced.

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2.2 First-Order Phase Transitions in Liquids

The occurrence of first-order transitions between different liquid phases has long been known as a function of composition. Unmixing occurs when an initially homogeneous liquid separates into distinct phases in order to minimize the free energy, $G(X)$, where X is a compositional variable. However, the idea that chemically homogeneous liquids might experience first-order transitions between phases with distinct volume (density), entropy, and enthalpy parameters to minimize the free-energy function ($G(P, T)$) is less intuitively obvious. A typical view of liquid structure is based on a range of local structural environments engaged in rapid dynamic interchange and diffusional processes. However, the time-averaged and spatially averaged structures related to macroscopic thermodynamic properties such as H , S , V , and G are fully defined for the thermally equilibrated system. It is reasonable to envisage distinct liquid phases with a different range of local structural states and thermodynamic parameters, as atomic packing and bonding requirements respond to changing P and T conditions. The $G(P, T)$ curves for any two such liquids would then cross at a particular set of P_{tr} , T_{tr} values as the system seeks to minimize its free energy, resulting in a first-order LLPT.

The locus of P_{tr} , T_{tr} values plotted in P – T space terminates at a critical point (P_c , T_c). Thermodynamic analysis suggests that in most cases such a critical point exists below the melting line, so the phenomenon is typically observed only in the metastable supercooled liquid state.

The physics of density- and entropy-driven LLPT are well recognized for liquid helium in which quantum effects play a determining role. They are also used to describe liquid sulfur (covalently bonded chains and rings) and organic polymer systems where the balance of forces between covalently bonded chains with ionic head–tail groups results in liquid crystalline behavior. The general occurrence of density- or entropy-driven LLPT within liquids at constant chemical composition was predicted by E. Rapoport who extended the model of regular solution thermodynamics based on nonideal mixing of components with different partial molar volumes developed by E.A. Guggenheim to understand and interpret the unusual negative melting relations found among certain substances [1]. A similar approach was developed by L.I. Aptekar in order to explain the negative melting slopes of Si and Ge [2]. Aptekar's expression for the free energy of the liquids was derived from a general treatment of two level systems by S. Strässler and C. Kittel that considered the degeneracy of excitations above a ground state to predict and rationalize the order of a phase transition. This approach forms the basis for later “bond-excitation” models that have been used to describe the occurrence of an LLPT.

2.3 Melting Curve Maxima and Two-State Models

Most crystals exhibit a positive variation of the melting temperature T_m with pressure because the entropy change upon melting (ΔS_m) is positive as a result of the larger configurational entropy of the disordered liquid phase. Liquids also typically have a larger molar volume than isochemical crystals, so the melting volume ΔV_m is positive. The Clausius–Clapeyron relationship ($dT_m/dP = \Delta S_m/\Delta V_m$) then implies that T_m increases with pressure. Exceptions to this rule include the elements Si, Ge, Ga, Sb, Bi, Ti, and Pu and diverse compounds such as H_2O , InSb, and Li_2MoO_4 . In each case, however, the initially negative melting slope is followed by a normal dT_m/dP relation as a phase transition to a denser crystalline solid takes place. Maxima also occur in the melting relations for systems including the metallic elements Rb, Cs, Ba, and Eu; nonmetals such as I, S, Se, Te, P, Sb, and C; and compounds including PbTe, Bi_2Te_3 , KNO_3 , $NaClO_3$, Na_2SeO_4 , and KH_2AsO_4 . Explaining these anomalies required a new approach to understanding liquid-state structure and melting thermodynamics [3, 4].

Rapoport accounted for these unusual melting properties by observing that the density-driven phase transitions occurring below the melting line typically involve an increase in local coordination number or a change in the interatomic bonding. He thus proposed that the liquid contains a mixture of structural units from both types of crystalline phase whose relative proportions change continuously as pressure increases. Unlike in the crystal, the concentration of high-density units builds up continuously, so above a certain pressure the liquid density exceeds that of the underlying crystal and the $T_m(P)$ relation exhibits a maximum. If this maximum occurs under negative pressure, in a tensile regime, then an initially negative melting slope is observed as is the case for Si, Ge, and H_2O .

Rapoport treated these low- and high-density domains, or species, within the liquid as thermodynamic mixing components with partial molar volumes V_L and V_H , which could be estimated from the volumes of species contained within crystals or molecular cluster models. The relative proportion of each species is expressed as mole fractions (x_L , x_H) with $x_H = 1 - x_L$. Such “two-state” or “two-species” liquid models had already been considered previously, notably for H_2O where the liquid was suggested to contain a mixture of H-bonded and non-H-bonded regions with dynamic interchange between the two. In models of this type, it had generally been presumed that the mixing relations would be expressed by entropic contributions alone. Because of cooperative effects on the bonding overall along with interface energy contributions, however, Rapoport considered that an

energy (enthalpy) gain or penalty should arise from the simultaneous presence of the different structural species within the liquid state. With a simple regular solution model, the free energy of mixing for the two-state liquid then became

$$\begin{aligned}\Delta G_{\text{mix}} = & RT[x_L \ln x_L + (1 - x_L) \ln (1 - x_L)] \\ & + P[x_L V_L + (1 - x_L) V_H] \\ & + x_L(1 - x_L)W.\end{aligned}\quad (1)$$

Here R is the gas constant and T is the absolute temperature. The inclusion of the pressure-dependent term indicates that the relative proportions of low- and high-density species depend on compression, whereas the mixing parameter W denotes the magnitude and sign of the two-state contribution to the mixing enthalpy. The ΔG_{mix} function is minimized to obtain x_L at each P and T of interest and used to obtain the total liquid free energy $G_{\text{liq}}(P, T)$ for comparison with that of the crystal to calculate T_m as a function of pressure. Appropriate values of W are determined by comparison with experimental melting data. At high T a single minimum occurs, as expected for a homogeneous liquid phase, and the $T_m(P)$ relation develops a maximum as found experimentally. As the temperature is reduced, the ΔG_{mix} function develops two minima at different x_L as the temperature drops below a limiting value, indicating the onset of two-phase separation between LDL and HDL liquids containing different proportions of the low- and high-density species. The critical temperature at which the two minima appears is defined by

$$T_c = \frac{W}{2R}.\quad (2)$$

It varies as a function of pressure, resulting in a first-order phase transition line between the low- and high-density liquid phases of the same chemical substance. In his original paper, which sought mainly to develop a rationalization of melting curve maxima, Rapoport noted that “such separation into two liquids has, as yet, never been encountered and we therefore restrict ourselves to values of $W/kT < 2$ ” [1] (k being Boltzmann’s constant, i.e. R divided by Avogadro’s number). In fact this is precisely the LLPT phenomenon that is becoming recognized and discussed for a very wide range of liquid systems [3, 4].

Because the maximum mixing enthalpy $W/4$ is typically smaller than the melting enthalpy, ΔH_m , the LLPT generally lies below the melting line, in the supercooled liquid regime. Studies of LLPT are then experimentally difficult because the phenomenon finds itself in competition with stable and metastable crystallization, including precipitation of nanocrystals alongside the nucleation

events for LDL during cooling from the HDL phase. A notable exception to this behavior concerns the LLPT recorded for elemental phosphorus above the melting line under simultaneous high pressures and temperatures [5]. However, even this apparently non-controversial result raises new questions that are difficult to answer. The lower-density polymorph appears to be in a fluid, rather than a liquid, state: i.e. it lies beyond the liquid–gas coexistence line for the low-density molecular LDL phase. That observation then raises important thermodynamic points for future investigation concerning the topology of liquid–gas–fluid phase relations in systems containing a density- or entropy-driven LLPT.

The slope of the LDL–HDL transition is determined by a Clausius–Clapeyron relation. As $\Delta V_{\text{LDL–HDL}}$ must be negative, the main parameter is the entropy contrast between the low- and high-density liquid phases, containing both configurational and vibrational entropy components. Arguments can be advanced to suggest that the LDL–HDL transition might also generally have a negative dT_{LLPT}/dP slope [6], which appears to agree with observations for systems including H_2O , Si, Ge, and phosphorus, although it may not hold universally. The LLPT line then terminates at a critical temperature and pressure (T_c, P_c) determined by the respective enthalpy, entropy, and molar volume parameters of the liquid species, as well as by the strength of the mixing parameter W .

2.4 Relationship Between Liquid-Liquid Phase Transitions and Polyamorphism

In systems shown or suggested to exhibit an LLPT, the line of first-order phase transitions along with their associated spinodal curves can be extrapolated below the glass transformation range, so density- or entropy-driven LDA–HDA polyamorphic transformations mapping on to the LLPT are expected to occur (Figure 1). Substantial kinetic effects could also be present, including hysteresis resulting from overdriving the LDA–HDA transition as well as structural relaxation within both polyamorphs; such studies can help map out the location of the first-order LLPT and its spinodal bounds. However, polyamorphic phenomena can also be observed in certain systems that are not directly correlated with an LLPT, but instead represent the relative population or relaxation of different parts of the configurational energy landscape (CEL) that are accessed through different synthesis or processing pathways [7].

The two-state approach first investigated by Rapoport has now been made more general by incorporation of ideas derived from CEL interpretations of liquid properties [4]. In a version of the two-state model developed by Angell and Moynihan, liquids are viewed as being thermally “excited” from an ideal low-entropy ground state

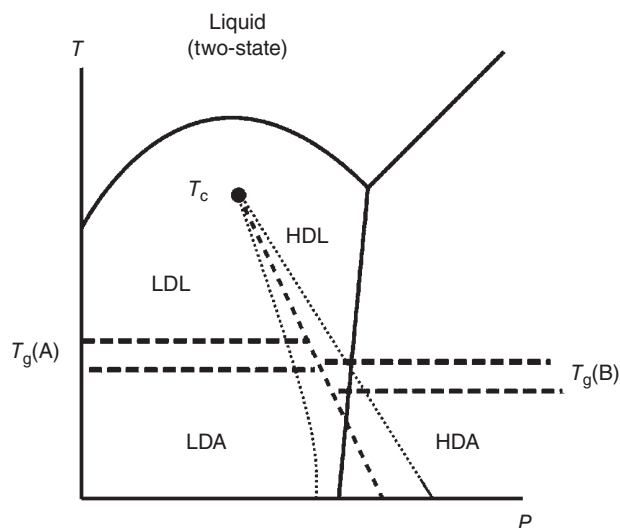


Figure 1 Schematic relationships between melting curve maxima, liquid-liquid phase transitions, and polyamorphism phenomena.

that would correspond to that of a hypothetical ideal glass. Upon heating bonds become broken, new structural environments appear, and the configurational entropy (S_{conf}) increases. Within such a “bond-excitation” model, S_{conf} vanishes when the fraction of excited or broken bonds is reduced to zero in an ideal ground state. For a fragile liquid the configurational entropy should vanish at a temperature below the usual glass transition observed experimentally, consistent with the existence of a Kauzmann temperature (T_K) at which the excess configurational entropy of a crystal vs. glass would disappear.

If the model is extended to include enthalpic contributions because bond-breaking processes affect the excess free energy in the system, then a nonideal mixing energy parameter (W) arises. If W is sufficiently large, then the entropy reduction and the resulting appearance of the ideal glassy form should take place via a first-order polyamorphic transition. A slightly different form of the two-state model has been championed by Tanaka. Here the liquid is assumed to comprise two competing effects: a “normal” one in which crystallization is driven by density-induced ordering and another in which the energetics are determined by locally favored structures. In this model the “strong” nature of substances such as silica is explained in terms of increasingly large fractions of locally favored structures as the liquids are cooled and vitrify. Then LLPT and polyamorphism effects result if mixing of the normal and locally favored fractions is treated as thermodynamically nonideal with a sufficiently large value of W . Both models envisage an approach to an ideal, low-entropy amorphous state and can be applied to all supercooled liquid systems irrespective of whether or not they are prone to polyamorphism.

Interesting questions are raised by the fact that different glass transition temperatures (T_g^L , T_g^H) link LDL and HDL phases to their corresponding LDA and HDA equivalents (Figure 1). During supercooling the LLPT from the HDL phase can be encountered at a lower temperature than T_g^L , resulting in direct production of the low-density LDA glassy polyamorph from the high-density liquid phase. Likewise, heating an HDA polyamorph metastably quenched from the liquid state by bypassing the LLPT would cause transformation into the LDA state during reheating to above T_g^H . Such complex situations require careful interpretation of the structural and thermodynamic observations associated with the various polyamorphic and liquid-glass transformation events.

It is interesting to note that extension of the melting line into the supercooled regime and beyond, below the glass transformation range, leads to prediction of a metastable “melting” event, involving a direct transformation of a crystal into an amorphous solid during compression. This phenomenon termed “pressure-induced amorphization” (PIA) was first predicted and observed for H_2O (ice Ih phase), where it led to identification of a polyamorphic transition between HDA and LDA forms of amorphous ice [8, 9]. Because PIA occurs in a wide range of systems, it now constitutes an important area of materials physics investigation along with LLPT and polyamorphism ([2, 10], Chapter 3.10).

2.5 Observations of Polyamorphism in Glasses and Amorphous Solids

Depending on synthesis procedure, the existence of different varieties of an amorphous substance is a well-known phenomenon in materials science [7]. For example, amorphous SiO_2 samples prepared from melts quenched at different rates, sol-gel synthesis, neutron irradiation, PIA of crystalline quartz, and thermal destabilization of metastable stishovite have different values of the density, refractive index, and other properties. These observations have been linked to the presence of different populations of various structural units within the glass. Crystalline SiO_2 exhibits several polymorphs with different linkage patterns between the tetrahedral SiO_4 units, whereas defects including broken bonds ($\equiv\text{Si}^+-\text{O}-\text{Si}\equiv$), SiO_5 species (i.e. five-coordinated Si), and high-energy three-membered siloxane rings can appear within the amorphous state. Identifying the nature of the primary linkage patterns and the presence of defects has thus formed a large part of the discussion concerning the structure of vitreous SiO_2 as well as other well-known glasses.

Lebedev proposed that changes in the structure and properties of glasses during annealing might be

understood as analogs to the phase transitions that occur between crystalline polymorphs (e.g. among different forms of silica) [11]. That suggestion was made against the background of discussions concerning the fundamental structure of glassy materials, including “continuous random network” versus “quasicrystalline” models. Studying amorphous solids produced from crystals exposed to intense radiation and particle beams, Kreidl and co-workers introduced the concept of “amorphous polymorphs” to differentiate them from normal SiO_2 glass quenched from the liquid. In a footnote to an article describing the glass-forming ability of aqueous electrolytes, Angell and Sore discussed the possible existence and identification of distinct “vitreous polymorphs” for an amorphous substance. The concept of polymorphism in glasses was described theoretically by Landau and Nikolaeva, and the term “polyamorphism” was coined to describe the existence of different amorphous states with characteristic physical properties, by analogy with crystalline polymorphism [12]. The term was reintroduced by G. Wolf et al. to describe distinct structures adopted by vitreous GeO_2 as a function of the pressure [13]. Previously, the concept of glassy polymorphism had also been invoked to describe and interpret changes in the mechanical properties of SiO_2 glass during annealing and as a function of pressure cycling.

2.6 High-Pressure Studies of Glass

The effects of pressure on glass properties and structure have been investigated since the pioneering studies carried out by Bridgman and Simon. Up to approximately 10 kbar (1 GPa), most glasses show a typical elastic response similar to that demonstrated by crystalline solids. As the pressure is increased into the 5–10 GPa range, however, “permanent” densification is observed in glasses recovered to ambient conditions, accompanied by changes in physical properties and structure revealed by diffraction and spectroscopy studies, as well as by computational modeling.

As followed *in situ* during densification studies or thermal treatment, the observed changes in structural parameters or physical properties can occur over quite narrow pressure or temperature intervals and be associated with hystereses that depend on the timescale of the experiment. In some cases, the structural changes recorded can be reminiscent of those of the crystalline phase transitions that occur in similar P , T ranges. These observations then raise important questions about the fundamental nature of the polyamorphic event being studied. Is it mainly a more or less gradual change occurring within a macroscopically homogeneous amorphous “phase”? Or does it instead represent an amorphous analog of a crystalline or LLPT, with metastable coexistence

of distinct components, each having its own stability domain within the P , T space and being potentially separable macroscopically? Evidence for both types of interpretations is found among different classes of amorphous substance and even for the same substance studied under different conditions.

Glasses typically contain a range of structural units, including species and local coordination states, which are not found among crystals. Changes in glass structure and properties can occur more or less gradually as pressure and temperature are varied and can be reinforced by continued cycling. Such polyamorphism can be understood as continuous changes in the glass structure occurring as different aspects of an overall configurational energy surface are accessed through either different synthesis and processing approaches or different P , T annealing conditions within the internally non-equilibrated solid. However, polyamorphic transformations can also exhibit characteristics that suggest the presence of an underlying thermodynamic phase transition. They can also be accompanied by the development of interfaces between different amorphous forms, which can even be physically separated in certain cases. These phenomena can generally be correlated with an LLPT occurring (or expected to occur) within the stable or supercooled liquid equilibrium state. They imply the presence of an enthalpic barrier within the CEL separating different “basins” that correspond to the two liquid phases [3, 4, 10]. It is thus important to develop an understanding of the CEL interpretation of glassy and liquid structures.

2.7 Configurational Energy Landscape Interpretations

For a system of bound or interacting particles, the CEL is a multidimensional representation of the energy (free, enthalpic, or potential) determined by all possible relative arrangements of the particles. It is usually sketched as a “funnel” plot, where the energy is represented as a function of two selected interparticle coordinate dimensions or as a slice through the system following a pathway through the configurational coordinates (Figure 2).

Most configurations are highly unstable and constitute a high-energy background of multiple energy states. More stable configurations tend to define a “funnel,” leading to the lowest energy states of the system. Single configurations corresponding to crystalline atomic arrangements lead to sharp negative peaks in the energy surface: the most stable crystalline phase has the lowest free energy at a given set of P , T conditions, typically separated by high barriers from those of other crystalline phases that must be crossed via potentially multiple pathways as the P , T and other physical parameters are changed. The liquid phases of the system occupy a number of

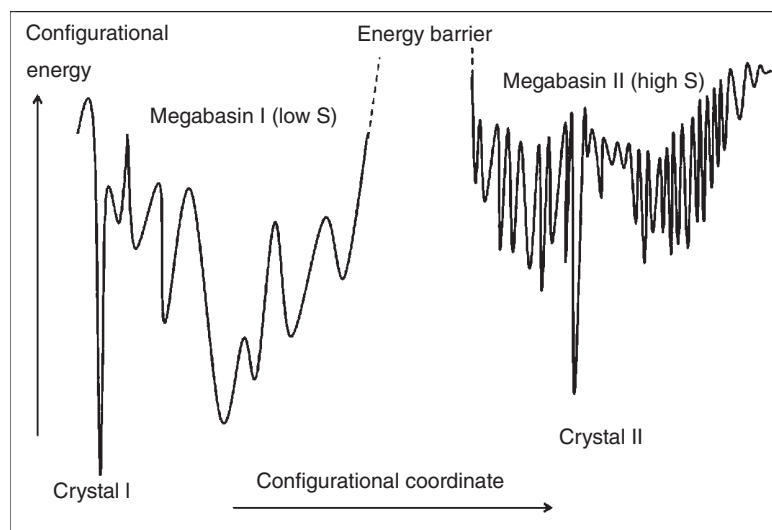


Figure 2 Schematic depiction of a configurational energy landscape along a one-dimensional pathway through the multiconfigurational space defined by all possible interatomic and intercluster interactions in the system. At left is shown a relatively sparse range of configurations with energy minima separated by relatively high local barriers. Thermal population of a selection of these gives a low-entropy liquid or solid amorphous or glassy state if the energy is removed too rapidly to achieve a global energy minimum. The stable crystalline phase at the pressure of interest is denoted by a single deep, sharp minimum representing its single structurally ordered configuration. The “ideal glass” configuration might also be achieved as a material having no long-range crystalline order but minimal configurational energy resulting from a balance between long- and short-range ordering effects. At right appears a different set representing configurations that occur at higher interatomic density, expected to result in a larger number of minima separated by smaller barriers between them. These constitute a higher entropy solution to the amorphous solid. The two “megabasins” are expected to be separated by a high enthalpic barrier that can give rise to LLPT in the stable and supercooled liquid states.

energy minima that are equally filled under equilibrium conditions. The number of such minima that are accessed determines the configurational entropy (S_{conf}) to the liquid free energy. High-entropy liquids typically have a high density of configurational states that are readily accessed via low-energy barriers; they constitute the “fragile” liquids recognized by significant deviations of their viscosity from Arrhenian laws. Strong liquids have a lower density of configurational states available or high-energy barriers needed to access them. When thermal energy is removed, not all the minima are equivalently occupied, as the system becomes non-ergodic or “glassy.” Different interatomic configurations are preferred according to the T -quench rate, subsequent annealing conditions, or other glass synthesis and post-synthesis processing parameters. This picture can provide an interpretation of glassy “polyamorphism” as different local atomic configurations contribute in different ways to the overall structural state.

Upon compression, bringing the atoms closer together induces changes in the CEL topology that are determined by the relevant interatomic potentials. Crystal–crystal phase transitions are then made possible when the relative energetics of the different crystalline minima vary. In first-order transitions substantial free-energy barriers between the two phases persist, and the transformation pathways from one to the other phase involve multiple configurational components. Second-order phase transitions

proceed via uniquely defined pathways in coordinate space, with energy barriers that vanish as the CEL becomes modified under the new set of thermodynamic P , T conditions. Given the wider range of closely separated configurational minima, such second-order transformations could potentially occur in amorphous substances, but they must typically lose the sharp structural and thermodynamic definition among transformation pathways achieved among crystals. To date, no amorphous–amorphous transformations have been clearly identified as corresponding to phase transitions of a second-order character.

Within the CEL interpretation, different possible aspects of polyamorphism can be recognized. First of all, a different range of CEL minima will be occupied to a different degree depending on the mode of preparation of the glass or amorphous solid, resulting in a different spatially averaged structure and set of physical properties being recorded. In addition, different preparation methods such as PIA or irradiation of crystalline substances could result in CEL with different topologies. When temperature is increased, or as thermal annealing proceeds, internal structural relaxation takes place as the population of different minima tends to become more equilibrated. If pressure is applied, the CEL will change more or less rapidly, the minima associated with denser configurations appearing or becoming deeper and the pathways linking different configurational states becoming altered. The result could be a rapid, if not abrupt,

change in the concentration of certain structural features and physical properties, which could be described as “polyamorphism.” However, a polyamorphic transformation that might be mapped on to an LLPT should involve traversing an enthalpic barrier separating two regions within the CEL, each representing different amorphous basins containing multiple minima. The density of accessible minima at a given temperature represents the configurational entropy of each amorphous basin, and, as a function of pressure, one or another polyamorph will be energetically favored at low or high density (Figure 2).

3 Classic Systems Exhibiting Polyamorphism

3.1 H₂O: Thermodynamic Anomalies, PIA, and High- to Low-Density Polyamorphs

Liquid water is a remarkable substance with outstanding structural, physical, and thermodynamic properties relevant to materials, planetary, and biological science. It exhibits unusual effects such as a density maximum at 4 °C, a higher density for the liquids than for the crystalline ice Ih phase, and a melting relation with a negative slope between room pressure and 200 MPa. Crystalline ice contains H₂O molecules linked into a three-dimensional network by hydrogen bonding, resulting in an asymmetric, approximately tetrahedral geometry around each oxygen atom. Upon melting a fraction of the H bonds are broken and the structure collapses, resulting in the higher density of the liquid phase. A two-structured “flickering cluster” model for liquid water emerged in which H-bonded domains existed within a matrix of less associated H₂O molecules, the two undergoing dynamic exchange with each other.

Because of the rapid kinetics of proton exchange, solid amorphous H₂O can only be produced by extreme methods such as very rapid cooling rates from the liquid state. Amorphous solid H₂O was first prepared in what is now known as the low-density amorphous (LDA) form by the deposition of water vapor onto a cold substrate or by rapid cooling of micrometer-sized droplets of liquid water. In 1984, Mishima et al. carried out a key experiment to transform the crystalline phase directly into amorphous H₂O by compressing the solid at low temperature in order to intersect the metastable extension of the melting line [8]. This successful study revealed a textbook example of the phenomenon of “pressure-induced amorphization.” However, Mishima et al. noted that the amorphous H₂O produced existed in a previously unknown HDA form and that it could be transformed back into the LDA polyamorph by annealing at low pressure [9]. The transformation was abrupt, thus resembling a first-order crystalline phase transition. This feature has

become recognized as one of the classic manifestations of a polyamorphic transformation.

To investigate the anomalous properties of liquid water in its metastable supercooled state, Poole et al. devised a series of molecular dynamics (MD) simulations with a potential energy function that contained not only the primary energy minimum to model O–H covalent bonding but also a subsidiary minimum at longer distances to mimic the effects of hydrogen bonding. The results were remarkable. As thermodynamic properties were tracked to lower temperature within the supercooled state, emerging anomalies suggested the onset of a phase transition between different forms of water with high (HDL) and low (LDL) densities. These two liquid phases with different densities and entropies related to their structural arrangements could then be linked to the HDA and LDA forms and to the polyamorphic transformation observed between them in the non-ergodic solid amorphous state [14]. This work has stimulated efforts to observe and characterize the implied first-order LLPT that should take place within the supercooled liquid state of H₂O. Studies of bulk samples are hampered by rapid crystallization events that occur during supercooling from the liquid or heating of solid amorphous ices such that a “no man’s land” region has been designated in that region of the metastable phase diagram expected to link the two states of matter. Studies of water confined within nanoscale environments, along with experiments conducted at fast (picosecond) timescales, are now beginning to probe the structural nature and phase transformations of liquid water in this highly metastable regime. It must be noted that not all authors agree that an HDL–LDL LLPT actually occurs within the metastable phase diagram of supercooled liquid water, although recent simulations and experimental results point to its existence [14, 15]. Likewise, the complexity of polyamorphic transformations occurring within solid amorphous ice is being revealed by new experiments and simulation studies [4, 14, 15]. Neutron scattering experiments first suggested the occurrence of a “very high-density amorphous” (VHDA) state linked to the presence of a second polyamorphic transformation. Later studies indicate that this apparently new polyamorph could in fact be associated with a continuum of structural states existing as a function of annealing conditions. Linking metastable H₂O liquid behavior with the observed polyamorphism remains one of the great challenges of physical science [16, 17].

3.2 SiO₂, GeO₂, and BeF₂

Early work that led to development of the concept of polyamorphism arose from consideration of the structure of vitreous SiO₂. With its structure based on corner-linked SiO₄ units, this substance constitutes one of the main archetypal glass-forming systems. Crystalline varieties of

SiO₂ exhibit substantial polymorphism thanks to the different linkage patterns available, which vary as a function of the density. Different amorphous “polymorphs” are obtained by following different synthesis routes and annealing procedures. Different amorphous varieties are also produced by techniques ranging from sol–gel synthesis to intense particle or electromagnetic beam irradiation and PIA of crystals. These amorphous forms have distinct structural signatures and physical properties while maintaining an underlying structure based on tetrahedrally bonded framework motifs. Studies have recorded apparent transformations occurring between different silica “polymorphs” as the P , T or annealing conditions are varied. However, the structural and physical differences between the different amorphous forms more likely to correspond to gradual modifications within the same underlying CEL, rather than to completely different amorphous basins or landscapes accessed by surmounting an enthalpic barrier between different polyamorphic “phases.” As pressure is increased, the dense SiO₂ phase stishovite and other octahedrally bonded crystalline polymorphs become stabilized. This raises the prospect of glassy polyamorphism between tetrahedrally (SiO₄-based) and octahedrally bonded (SiO₆) structures.

The results and arguments for LDA–HDA, LDL–HDL, and related metastable transformations have been extended to other tetrahedrally bonded amorphous framework systems such as GeO₂ and BeF₂. In the case of GeO₂, there is clear evidence for density-driven polyamorphism associated with two-state behavior [13]. However, the existence of a critical point linked to a LLPT and pressure-induced polyamorphism in supercooled liquid SiO₂ at experimentally achievable temperatures is now being questioned from computer simulation studies [18]. Deciphering the occurrence and nature of polyamorphism phenomena in this classic series of glass-forming materials remains an active area of materials research.

3.3 Amorphous Semiconductors: Si and Ge

Like H₂O ice Ih, the elements Si and Ge both exhibit a negative $T_m(P)$ melting slope at low pressure. The diamond-structured semiconductor Si melts to form an electrically conducting liquid, which contains five- and six-coordinated structural species according to X-ray and neutron scattering experiments and MD simulations. Amorphous Si is a well-known semiconductor produced by vapor deposition techniques. It has a tetrahedrally bonded structure similar to the crystalline solid, but containing various broken bond or other structural defects. Rapid thermal analysis experiments suggested a metastable “melting” event located below the thermodynamic crystal–liquid transition temperature, by which the

LDA solid amorphous semiconductor transformed directly into the HDL metallic liquid. Recent fast time-scale experiments have clearly identified a glass transition linking the LDA with its supercooled LDL liquid. MD simulations and application of thermodynamic two-state liquid models indicate that an LDL–HDL LLPT event occurs in the metastable supercooled liquid regime [19, 20]. The critical (T_c , P_c) values are predicted to appear at slightly negative pressure, i.e. under tensile conditions of approximately –5 GPa.

Upon room-temperature compression of a porous variety of crystalline Si, Deb et al. observed PIA occurring above 14 GPa, resulting in an HDA form of a-Si. During decompression to ambient conditions, the structural signature of the normal LDA tetrahedrally bonded semiconductor reappeared. The results were analyzed in terms of PIA leading to the HDA polymorph above the upper spinodal line associated with the LLPT extended metastably below the glass transformation range, followed by back-transformation into the LDA form at the lower spinodal bound during decompression. The existence of an LDA–HDA transition was tested by pressurization studies of LDA a-Si combined with electrical conductivity measurements, as well as synchrotron X-ray and Raman scattering studies (Figure 3). The results mapped out an hysteresis for the polyamorphic transformation event consistent with theoretical modeling [20]. An analogous

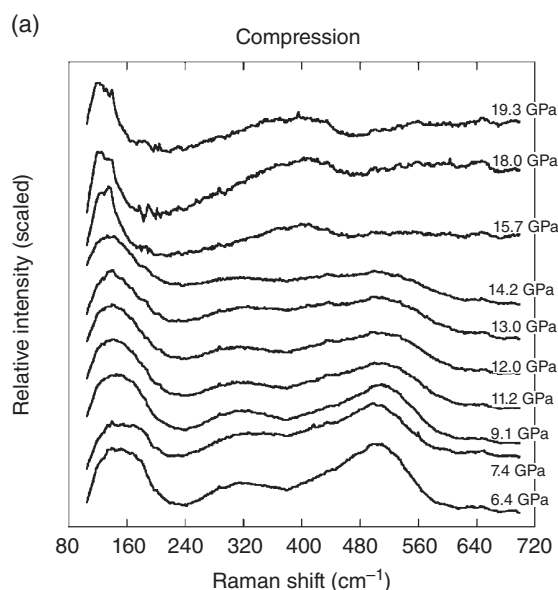


Figure 3 Polyamorphism in a-Si upon compression and decompression. (a) Abrupt change in Raman spectra showing the transition from the tetrahedrally bonded LDA state to the metallic HDA polyamorph above 14 GPa. (b) Back-transformation from HDA to LDA below 8 GPa also visible in Raman spectra. (c) Mapping out of this reversible polyamorphic transition by electrical resistance measurements carried out in the diamond anvil cell. All pressures indicated in GPa.

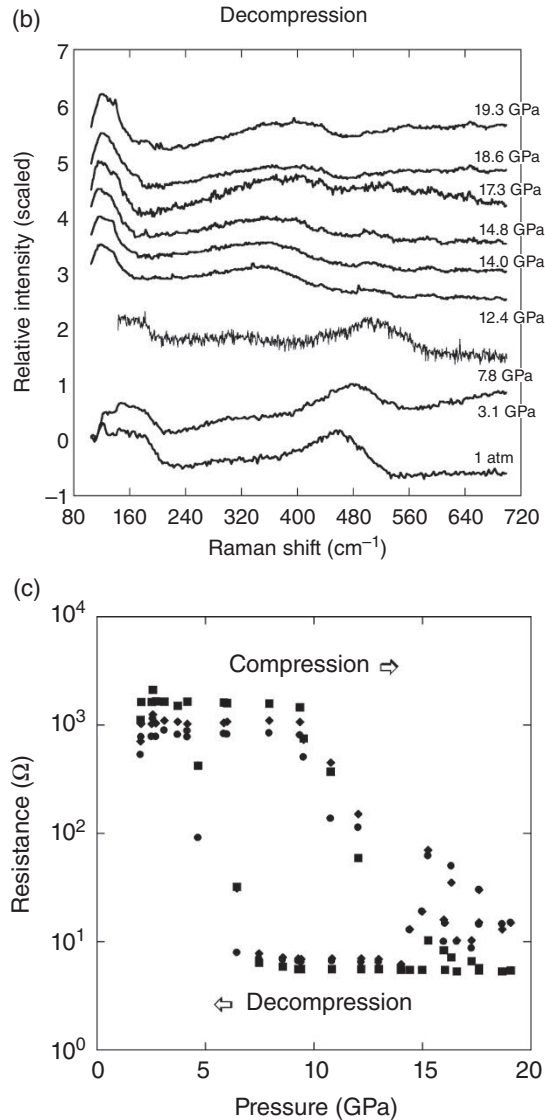


Figure 3 (Continued)

high-pressure study of a-Ge by Barkalov et al. revealed superconductivity occurring in the HDA state, whereas Bhat et al. have quenched the high-pressure liquid to form a high-density metallic polyamorph.

The structural properties and relaxation dynamics within the high-*T* liquids have been probed by synchrotron X-ray scattering on levitated samples in a containerless regime and by MD simulations. The experiments revealed a gradual change in average Si coordination as the temperature was lowered, but no LLPT could be observed because of rapid crystallization in the supercooled regime. Likewise, MD simulations could not reveal directly the nucleation and growth of a second liquid phase, although anomalies developed in the thermodynamic properties indicated the approach to an LLPT.

Simulations carried out at temperatures approaching that of the LLPT revealed random volume variations occurring around the low- vs. high-density equilibrated states. These variations signal that the system is sampling HDL and LDL configurations within the CEL above the LLPT critical point. First-principles liquid state calculations show development of a sigmoidal shape in *P*–*V* isotherms indicating a transition between semiconducting (LDL) and metallic (HDL) forms. In the case of liquid Ge, Bhat and co-workers demonstrated that rapid quenching of a sample formed at high pressure in a diamond anvil cell resulted in formation of the HDA metallic polyamorph. These combined experimental, simulation, and thermodynamic modeling results clearly indicate the presence of LDA–HDA polyamorphism associated with an LLPT between LDL and HDL phases in the supercooled liquid regime for these technologically relevant systems. It is now of interest to explore and extend the manifestation of these polyamorphic events into binary Si–Ge and more complex systems based on elemental alloys within groups 13–15 of the periodic table.

3.4 Polyamorphic Transitions in the Y₂O₃–Al₂O₃ System

During studies of metastable crystallization and melting within the ceramic Al₂O₃–Y₂O₃ system, Aasland and McMillan first observed nucleation and growth of a second liquid occurring within the supercooled high-temperature liquid phase during quenching. Both liquids were arrested by the glass transition, so recovered samples contained coexisting glasses [21]. This phase separation was recorded for compositions ranging between 20 and 35 mol % Y₂O₃. In each case, the recovered glasses had experimentally indistinguishable chemical compositions, but their structures appeared to be different in microbeam Raman and FTIR spectroscopy experiments (Figure 4). In addition, backscattered electron imaging revealed a density difference between the LDA and HDA regions. The result was interpreted as a case in which the supercooled liquid system had traversed an LLPT line during cooling, which caused nucleation and partial growth of an LDL or LDA phase within the supercooled HDL matrix, resulting in coexisting LDA and HDA glasses following the quench.

Polarizable-ion molecular dynamics (PIMD) studies were carried out during supercooling of model liquids to understand the onset of polyamorphism. As *T* was lowered toward the expected onset of the LLPT critical behavior, the simulations showed random jumps between low- and high-density states, which equilibrated around larger vs. smaller volume configurations providing evidence for dynamic sampling of the high- and low-density basins within the CEL above the LLPT. Experimental



Figure 4 Evidence for polyamorphism in $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ glasses. Optical microscope image of a polished sample obtained by quenching from a liquid with composition 20 mol % Y_2O_3 : 80 mol % Al_2O_3 (AY-20). During the quench segregated regions of LDA (top left) and HDA glassy material appeared with the same chemical composition. A clear interface between the two glasses is observed, and cooling cracks within the LDA phase do not extend beyond the boundary. The spherical shapes observed within the glassy regions represent gas bubbles and also LDA material exsolving within the HDL liquid matrix. The square outlines reveal the presence of YAG crystals formed simultaneously during the quench.

studies of supercooled $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ liquids were carried out using containerless levitation combined with small- and wide-angle X-ray (SAXS, WAXS) and neutron scattering studies. Greaves et al. interpreted the SAXS results to indicate nanoscale density fluctuations prior to formation of the LDL liquid, in agreement with the PIMD results. Barnes et al. contested these results, suggesting that the samples contained nanocrystalline phases. Recent work has reconciled the contrasting results in terms of differences in sample composition and relaxation timescales.

3.5 The Case of Phosphorus: Liquid–Liquid vs. Liquid–Fluid Transitions

In X-ray scattering studies of liquid phosphorus under high- P , T conditions, Katayama et al. observed a first-order LLPT occurring in the stable liquid regime between 1050 and 2200 °C and $P = 0.3\text{--}0.9$ GPa [5]. The X-ray data indicated that the transition took place between an LDL phase containing discrete molecular P_4 units and an HDL polymeric liquid. Patterns taken at the transition point clearly showed a superposition of patterns of the two phases, and hysteresis occurred as P and T were varied. Further studies of stable and metastable phase relations in the phosphorus system show that the transition in fact occurs between the HDL polymeric liquid and the LDL

monomeric phase in a fluid state, i.e. beyond its liquid–gas equilibrium line. This situation highlights the fact that each liquid polyamorph must possess its own liquid–gas–fluid equilibrium relations. Likewise, each low- or high- density liquid polyamorph possesses a separate glass transformation (i.e. T_g^H vs. T_g^L , linking high- vs. low-density liquid [HDL, LDL] and solid amorphous [HDA, LDA] states) that must be taken into account when designing probe experiments and analyzing data to study polyamorphism and LLPT behavior.

3.6 Triphenyl Phosphite

Triphenyl phosphite ($\text{P}(\text{OC}_6\text{H}_5)_3$: TPP) forms a molecular crystal with $T_m \sim 295$ K. The supercooled liquid constitutes a “fragile” glass-forming system with distinctly non-Arrhenian relaxation properties, which can be studied down to its T_g of approximately 190–205 K. If the liquid is annealed between 210 and 223 K, however, a new, apparently amorphous, solid “glacial” phase nucleates and grows [22]. Initially this transition was thought to be between the supercooled liquid, which represented an HDL phase, and the glacial form, which represents the LDA polyamorph produced via an LLPT below the LDL glass transition. So much effort has been devoted in unraveling and understanding the nature of the glacial form of TPP and its metastable transformation that such studies became a central part of discussions concerning polyamorphism. It is now thought that the glacial phase likely represents a metastable nanocrystalline material with significant structural defects and disorder, although arguments based on LLPT and polyamorphism in the system continue to be discussed. Certain authors believe that the glacial form results from an LDL or LDA polyamorph that nucleates and grows within a matrix of the supercooled HDL phase via a first-order density- or entropy-driven LLPT. The nature of the polyamorphic transition in TPP is still under discussion.

3.7 Metallic Glasses

Amorphous metallic systems such as a-Fe are important technological materials, but they typically require very rapid quench rates ($>10^6\text{--}10^7$ K/s) to be produced from the liquid phase. However, complex materials containing various metallic and nonmetal components yield bulk glasses through cooling at rates of only $10^2\text{--}10^0$ K/s. This contrast can be understood partly in terms of the informal *confusion principle* according to which ease of vitrification improves within multicomponent systems with increased configurational entropy, covalent bonding, and lack of efficient crystallization pathways. These bulk metallic glasses are developed commercially for applications requiring

high mechanical resistance and specific electronic and magnetic properties. Early work on the high-pressure, high-temperature phase relations of metals such as Cs, Eu, and Ce revealed melting curve maxima interpreted by Rapoport using two-state structural models for the liquids and leading to the concept of LLPT and polyamorphism. Now density-driven polyamorphism has been discovered in metallic glasses such as $\text{Ce}_{55}\text{Al}_{45}$ linked to changes in the $\text{Ce } f$ orbital manifold with increased atomic packing [23]. During studies of Zr–Cu–Ni–Al–Nb–Ti supercooled liquids, abrupt changes between “fragile” and “strong” rheology noted in the vicinity of T_g could suggest the possible presence of an LLPT. Such metallic glasses and glass-forming liquids constitute a new family of systems in which polyamorphic or LLPT behavior could have technological consequences.

4 Perspectives

Polyamorphism, LLPT, and PIA are mutually linked phenomena forming an integral part of condensed matter physics and chemistry that is only just beginning to be appreciated and understood. They can occur generally among a wide variety of stable and supercooled liquids and condensed amorphous states exhibiting all types of chemical bonding. The occurrence of LLPT can be correlated with polyamorphism observed among glasses and other non-crystalline solids, but amorphous polymorphs can also be observed when different configurational states are accessed by different synthesis or processing pathways. There is also the possibility for multiple LLPT and polyamorphic transformations to occur within a given system as a function of the density. The existence of multiple liquid forms of a given substance induces rheological changes whereby viscosity and diffusion properties are related to the density and configurational entropy. These connections have implications not only for materials research but also for matter relevant to Earth and planetary sciences.

Quenching high- vs. low-density polyamorphs that may coexist metastably and growing metastable nanocrystalline phases within one or other of the polyamorphs raise the possibility of creating new nanocomposite materials such as ceramics, polymers, and metals with unusual and useful properties. Polyamorphism can lead to insulator–semiconductor–metal transitions between amorphous forms of the same substance. Polyamorphic phenomena can also be recognized among the collective excitations found in magnetic and dielectric materials. Polyamorphism concepts can be applied to the macromolecular chemistry of polymers and biomaterials where the CEL provides a useful common framework to understand folding and unfolding of proteins, polypeptides, and other

large-scale molecular systems incorporating covalent, ionic, and H bonding along with hydrophobic vs. hydrophilic interactions. We expect that useful applications of such analogies will grow with our understanding of polyamorphic phenomena and metastable phase transformations in general.

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3.10

Pressure-Induced Amorphization

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1 Introduction

Crystalline solids exhibit phase transformations between different structural polymorphs as a function of applied pressure, and they also undergo a melting transition into a liquid phase as temperature is increased. For most substances cooling the liquid rapidly allows the system to bypass crystallization, and a structurally disordered solid glassy form is obtained. Such glasses have many technologically important properties and applications that are well documented. However, certain classes of materials including liquid metals; elemental Si, Ge, and Se; and H₂O generally crystallize too rapidly for vitrification to occur. In these cases amorphization is achieved by other routes, including condensation from the vapor phase on to cold substrates, chemical synthesis reactions or rapid precipitation from solution, expulsion of solvent molecules from host–guest lattices resulting in collapse of the crystalline framework, and large-scale defect formation via bombardment of crystals by high-energy particle or radiation beams [1]. A further approach is to subject the crystal to high pressure at temperatures too low to enable the thermally activated processes of nucleation and growth of stable or metastable crystalline phases. The result then is mechanical destabilization to a structurally disordered material that can resemble amorphous solids produced by thermal quenching or other means. This process has been termed “pressure-induced amorphization,” or PIA, and it has now been reported to occur among many different classes of materials

[2–5]. Another aspect of PIA that is particularly relevant for Earth and planetary science applications is partial or complete amorphization of minerals during shock compression [5].

2 First Observation of PIA: Metastable Melting vs. Mechanical Destabilization of Ice Ih

The occurrence of PIA during static compression was first predicted and observed for the ice Ih polymorph of crystalline H₂O, which was compressed metastably beyond its normal stability range at low temperature (77 K) [6]. It was already known that ice had a negative dT_m/dP melting slope, which might be extended metastably below the normal melting line to below the proposed glass transformation range. That observation led Mishima and colleagues to predict that a “cold melting” event could occur through a quasi-first-order transformation between the metastably compressed crystal and a glassy phase at sufficiently low temperature (Figure 1).

During compression of ice Ih at 77 K, a rapid reduction in molar volume was observed at approximately 1.1 GPa, and the solid material recovered at ambient pressure was found amorphous upon X-ray examination. Mishima et al. concluded that PIA had occurred at a pressure that corresponded approximately to the predicted crossing of the free energy curves of the metastably compressed crystal and the solidified glassy state. That observation and its interpretation have resulted in the emergence of a new research field linking crystalline, glassy, and liquid state physics. The PIA phenomenon was subsequently reported to occur among a very wide range of substances with all types of chemical bonding [2–4].

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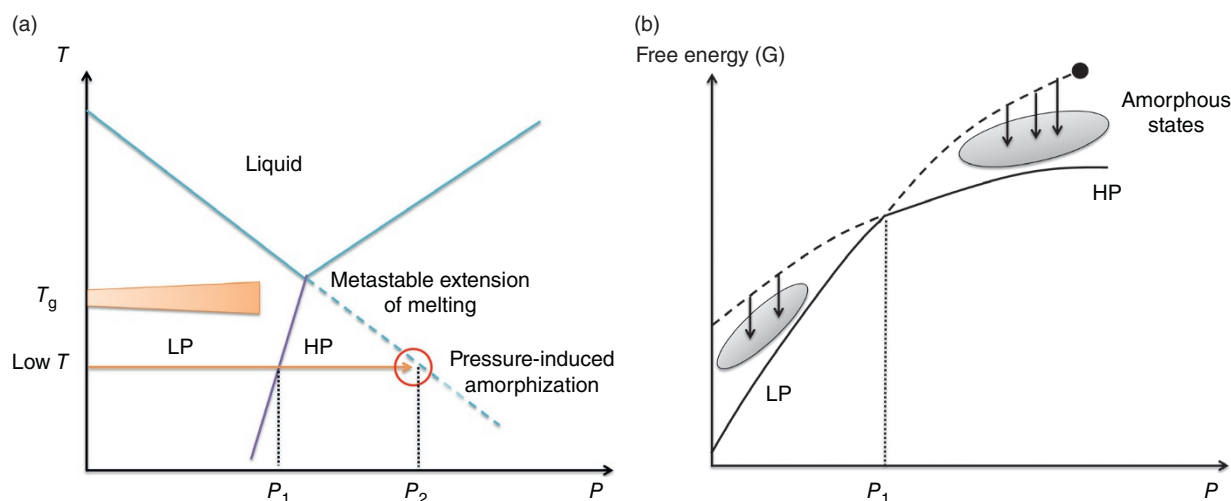


Figure 1 Two schematic representations of pressure-induced amorphization. (a) A metastable melting event can occur as the crystalline phase (LP) with an initially negative $T_m(P)$ melting slope amorphizes at P_2 and low temperature instead of transforming at P_1 to a denser (HP) polymorph. (b) The metastable extension of the free energy $G(P)$ curve for the LP phase must terminate at some critical value. If the thermal energy is low, the system will become trapped in a locus of amorphous states (shaded gray), and PIA occurs instead of transformation to the HP phase. Likewise, decompression-induced amorphization may occur as an HP phase is recovered metastably to ambient pressure conditions (second shaded area above LP curve).

Attempts to understand the microscopic nature of the events leading to melting of crystals have occupied condensed matter scientists for well over a century. Thermodynamically, melting and the reverse process of crystallization from the liquid state occur at equilibrium as the $G(P, T)$ free energy relations for the two phases cross. However, because a first-order transition is associated with an enthalpic barrier, substantial superheating can occur if nucleation sites for melting are absent. Likewise, liquid samples can be supercooled well below T_m until the onset of the glass transition, resulting in formation of an amorphous solid. An atomistic model developed by Lindemann first considered that thermal excitation of vibrational modes resulting in critically large atomic or ionic displacements caused collapse of the crystalline lattice. Other interpretations have suggested that development of critical concentrations of “defects” including thermally induced vacancies, interstitials, or dislocations culminate in lattice collapse and in the onset of atomic, molecular, or ionic mobility, leading to a molten state. L. Brillouin and M. Born both considered the intrinsic limits of crystal stability in terms of mechanical constraints and in particular their need to maintain a resistance against shear stress. The elastic criteria presented by Born lead to a maximum upper stability limit determined for a given crystalline state, as a function of applied temperature or pressure [7].

All of these approaches have now been applied to understand the nature of PIA. Closely following the original observation of the effect and its interpretation as a metastable melting event, Tse and Klein [8] proposed that

amorphization of ice Ih arises as a result of shear instability within the crystal [8]. Further work revealed that the complex amorphization process could involve aspects of both dislocation- or defect-induced mechanisms as well as crystalline shear or even localized phonon instabilities. Understanding the PIA phenomenon has thus now become part of much wider discussions concerning the fundamental nature of stable and metastable transformations between crystalline, liquid, and amorphous solid states of matter.

A key aspect of all this work is identifying the amorphous nature of solids produced as crystals are pressurized beyond their stability limits at temperatures too low to initiate nucleation and growth of high-density crystalline phases. Various techniques are used to probe the structural state of samples and diagnose amorphization effects. However, they differ in their sensitivity to different length scales and degrees of structural order, which can affect the diagnosis of a PIA event [3, 4]. The observation of PIA also depends on the hydrostatic vs. non-hydrostatic nature of the compression conditions and the timescale on which they are applied, as well as the chemical purity, crystallinity and grain size of the starting samples. In certain cases, PIA reported initially from experiments carried out under less than hydrostatic conditions has been countered by careful compression studies of single crystals. Typically these results have led to identification of new crystalline phases formed via metastable transformation pathways in the superpressed solid [9, 10]. It has also become obvious that it is not always easy to distinguish between fully amorphous and

nanocrystalline or bulk crystalline materials containing a high density of defects.

Shortly following the initial observation of PIA in ice Ih [6], it was noted that the “glassy” material produced corresponded to a new high-density amorphous (HDA) form that could be recovered metastably to ambient conditions. That result sparked a further new field of research into the phenomenon of “polyamorphism,” which is linked to the presence of density- or entropy-driven liquid–liquid phase transformations (Chapter 3.9). Other observations showed that high-density crystals prepared at high pressure and recovered metastably to ambient conditions can also amorphize upon heating [5, 11] and that some high-pressure phases suffered catastrophic failure of the crystalline lattice caused by phonon instabilities during decompression [12]. However it is interpreted or achieved, PIA and related phenomena result in new families of structurally disordered solids that can have technologically important properties, including novel nanocomposites [4].

3 SiO_2 and AlPO_4 : “Memory Glass” Effects

Shortly after the report of PIA for ice Ih, R. Hemley et al. reported a similar effect occurring for the SiO_2 minerals α -quartz and coesite [13]. These phases are structurally related to ice polymorphs with Si–O–Si bridges between tetrahedral SiO_4 units taking the place of H-bonded H_2O frameworks. Using *in situ* X-ray diffraction in a diamond anvil cell, they showed that the crystalline materials transform into amorphous solids between 25 and 35 GPa at ambient temperature and developed a similar interpretation to that of Mishima et al. in terms of a metastable “melting” event. Although neither quartz nor coesite exhibit a negative melting relation, the authors proposed that a maximum appears in $T_m(P)$ for both phases in the 0–10 GPa region, consistent with incipient crossing of the metastably compressed crystalline and glassy free energies below T_g . Later work proposed alternative interpretations of the SiO_2 amorphization event in terms of a crystalline mechanical instability, similar to that suggested for H_2O ice Ih [14]. However, careful compression of single-crystal quartz under quasi-hydrostatic conditions results in transformation into a metastable crystalline (quartz II) phase rather than in PIA [9]. A detailed analysis of PIA occurring for the isostructural α -quartz phase of GeO_2 has been discussed in terms of collapse of the tetrahedrally bonded crystalline lattice [15].

It is important to recognize that PIA, along with all other metastable structural transformations occurring

during low-temperature compression or on a rapid timescale, is subject to kinetic effects that hinder bond-breaking and bond-reforming processes as well as atomic or ionic diffusion that would lead to an equilibrium ordered state. In addition, the distribution of applied stresses external to or developed within the sample is important, as deviations from truly isotropic or hydrostatic compression can provide lowered energy pathways or local driving forces, leading to PIA. Slower compression of single crystals under quasi-hydrostatic conditions results in metastable crystalline transformations, whereas compression of powders under non-hydrostatic conditions or on rapid timescales can lead to PIA of the same substance [9, 10]. The characteristic sensitivity to local vs. longer-range structural order of the probe technique used to investigate the phenomenon must also be taken into account in diagnosing PIA events [4].

In the example of berlinite (α - AlPO_4), which is isoelectronic with and structurally analogous to α -quartz, PIA was initially observed at around 13 GPa in a surprising way since the transformation appeared to be fully reversible, apparently conserving the orientation of the original crystalline axes. This unexpected result was described as a “memory glass” effect [16]. However, later work showed that the high-pressure “amorphized” form of AlPO_4 produced under the non-hydrostatic conditions of the original experiment was in fact a disordered crystalline solid [17]. Angle-dispersive X-ray diffraction experiments performed up to about 100 GPa have now demonstrated a two-stage densification process in which a hexagonal oxide sublattice forms first within the material, followed by redistribution of Al^{3+} and P^{5+} among the cation sites [18].

4 SnI_4 and Cu_2O : Examples of Compositionally Driven Instability

A crystalline-to-amorphous phase transition in SnI_4 under pressure was first described with laboratory X-ray diffraction and Raman scattering techniques [19]. The transition was initially thought to involve only the initial cubic crystal phase, but this interpretation was challenged by the observation of a second crystal phase at about 7.5 GPa. The pressure-amorphized SnI_4 phase emerged above 15 GPa and then crystallized at 61 GPa to produce a new structure with an fcc lattice containing I_2 units. This suggested that internal molecular dissociation could provide a driving mechanism for the metastable transformation phenomena. The latest work reveals a complex series of disordering and recrystallization transitions driven by electronic effects and atomic packing considerations [19].

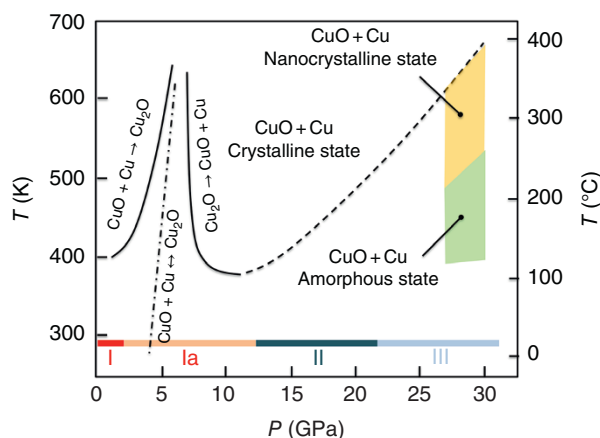


Figure 2 Phase diagram of Cu oxides in stable and metastable regions. At ambient temperature, the cubic(I)-to-tetragonal(Ia) phase transition is observed in the Cu_2O stability region, whereas the two structural transitions Ia–II and II–III occur in the metastable region. The solid curves show the kinetic lines of the $\text{Cu}_2\text{O} \rightarrow \text{CuO} + \text{Cu}$ decomposition and $\text{CuO} + \text{Cu} \rightarrow \text{Cu}_2\text{O}$ synthesis, and the dashed line shows the equilibrium between Cu_2O and $\text{CuO} + \text{Cu}$ line. Source: Diagram redrawn from the original data of Ref. [20].

At ambient temperature semiconducting Cu_2O exhibits various structural and chemical transformations up to 20 GPa. In the equilibrium phase diagram of copper oxides, the equilibrium pressure of the reaction $\text{Cu}_2\text{O} \rightarrow \text{CuO} + \text{Cu}$ is 4–5 GPa at ambient temperature (Figure 2). Heating metastably compressed Cu_2O polymorphs at 30 GPa leads to the following sequence of events: (i) at around 410 K, Cu_2O becomes amorphous and remains so at least up to 535 K; (ii) further heating to 670 K yields a nanocrystalline two-phase mixture of $\text{Cu} + \text{CuO}$; and (iii) prolonged heating at this temperature leads to the full crystallization of this mixture. This sequence provides further evidence for amorphization driven by high-pressure decomposition reactions [20].

Other studies have proposed that PIA in complex solids results from kinetically hindered decomposition or disproportionation reactions of an initially chemically homogeneous crystalline phase. This model has been advanced to explain PIA observed among the family of LiMSO_4 compounds, where M is an alkali metal. The compound LiNaSO_4 does not undergo amorphization under pressure, whereas other members of this family do. One explains this result by noting that the combined volume of the decomposition products (Li_2SO_4 and M_2SO_4 , with $\text{M} \neq \text{Na}$) is smaller than that of the parent phase. However, more recent synchrotron X-ray diffraction studies have shown that LiKSO_4 in fact transforms to a high-pressure polymorph without any evidence for PIA, even under non-hydrostatic stress conditions [4].

5 Nanocrystalline Materials

At the nanoscale, materials exhibit physical and chemical properties that are different from those of the bulk crystals because of large surface/volume ratios. The thermodynamics and mechanical stress/strain relationships within nanoparticles are thus largely determined by surface free energy effects. The energetic contribution from electron quantum confinement also contrasts with a bulk band-structure description of the electron energy levels. The contribution of the surface energy can stabilize new polymorphs at ambient conditions and result in new properties. For example, the important semiconductor TiO_2 adopts a rutile structure in its bulk phase, whereas TiO_2 nanoparticles crystallize with the anatase structure; these nanoparticles are widely used for their photocatalytic properties. Another striking example of phase equilibria modified by surface effects is the melting process. The melting point depression observed for small particles has been known since the latter part of the nineteenth century and is described by the Gibbs–Thomson equation (i.e. J.J. Thomson, not W. Thomson, later Lord Kelvin) and derived in its modern form by F. Meissner and E. Rie. From a microscopic view, melting has been correlated to chemical disordering induced by point defects via a generalized adaptation of the Lindemann melting criterion. In nanoparticles, the surface considered as an extended defect is associated with a positive excess entropy, which is augmented further if the surface is defective. This leads to stabilization of the liquid or a solid amorphous phase below the glass transformation range, so both the kinetics and thermodynamics of melting or PIA are affected. Nanocrystals can also readily be prepared with few or no internal defects, and experiments show that they can be superpressed until the mechanically unstable elastic limit of the initial crystalline phase is reached. The resulting material is observed to be amorphous if there is insufficient thermal energy within the system to enable new crystalline structures to nucleate and grow.

In the case of the technologically important elemental semiconductor Si, PIA does not occur for the bulk crystalline material, but the phenomenon was observed for a porous nanocrystalline variety of p-doped π -Si compressed above 10 GPa at room temperature [21]. The onset of amorphization was recorded as a broadening and loss of the (111) nanocrystalline peak observed by energy-dispersive X-ray diffraction, whereas the Raman spectrum showed a fully amorphous broad signature by 12 GPa (Figure 3). Interestingly, the Raman spectrum did not correspond to that of a typical a-Si material based on tetrahedrally bonded units but instead resembled the vibrational density of states of a highly coordinated

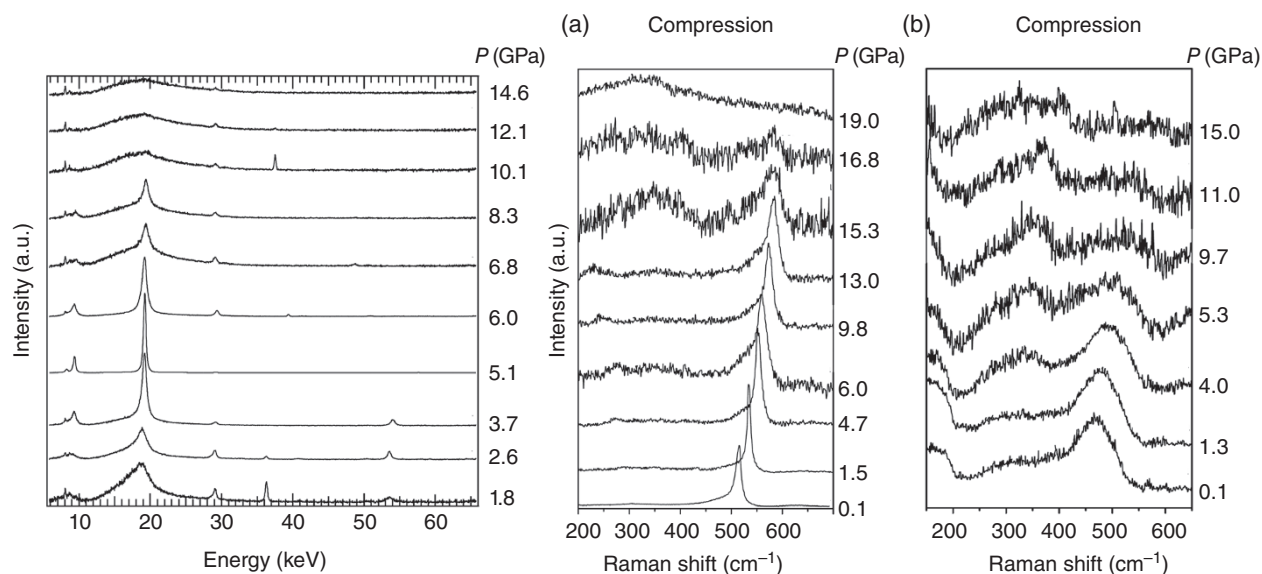


Figure 3 Evidence for pressure-induced amorphization in nanoporous crystalline silicon. Left: Energy dispersive X-ray diffraction patterns showing initial sharpening of the principal (111) peak of the diamond structure followed by substantial broadening and finally disappearance of the crystalline diffraction above 10 GPa. Right: Raman spectra for porous Si at high pressure. During compression (a) the crystalline peak is replaced by the broad amorphous signal above 13–16 GPa from the HDA form of amorphous silicon. During decompression (b) the Raman spectrum for tetrahedrally bonded LDA a-Si emerges below approximately 5 GPa. Source: Data redrawn from [21].

metallic crystalline form such as Si-II (β -Sn structure). It was concluded that PIA had resulted in direct transformation into the HDA polymorph, which then back-transformed into the low-density amorphous (LDA) form of a-Si during decompression (Chapter 3.9). However, a more recent investigation of π -Si compression with Raman spectroscopy and angle-dispersive X-ray diffraction provides a slightly different view of the metastable transformation events [22]. The X-ray diffraction results indicate that metastably compressed π -Si transforms to the primitive hexagonal crystalline phase at about 20 GPa, which does not have a first-order Raman spectral signature. However, formation of the HDA form of a-Si was confirmed during decompression of the high-pressure phase, whereas the HDA–LDA transformation occurred at around 4.5 GPa, as observed initially. Recompression of the LDA state led to the transformation to the primitive hexagonal structure around 18 GPa. This reversible transformation proceeds via an HDA state.

The reversibility of the amorphous-to-crystal transition in nanomaterials under pressure has been discussed in terms of the nanocrystalline nature of the HP phase and an increase in Gibbs free energy associated with disorder at the grain boundaries [23]. Below a critical particle size, pressurized nanomaterials including TiO_2 , Y_2O_3 , and PbTe exhibit a crystal-to-amorphous transformation instead of their expected polymorphic crystalline phase transition. This observation highlights a greater propensity of

nanomaterials for amorphization that depends on the defect density and interfacial energy, which can be controlled by appropriate synthesis approaches.

6 Zeolites as Examples of “Perfect Glass” Formation

The idea of a “perfect glass” with a vanishingly low configurational entropy was first introduced by W. Kauzmann (Chapters 3.1 and 3.2). The arrest of atomic dynamics at the glass transition during cooling generally precludes formation of such a “perfect glass” state. However, structural collapse engineered by metastable compression of open-structured microporous materials such as zeolites provides an alternative route to prepare amorphous solids where thermally activated interdiffusion of ions or molecular species is not an issue. This approach to a “perfect” glassy state has indeed been followed through PIA of zeolites [24]. Typically zeolites consist of fully corner-connected $(\text{Al,Si})\text{O}_4$ tetrahedra, leaving cavities and channels of various sizes occupied in most cases by extra-framework charge-balancing cations or water molecules. The low-density microporous structures are already metastable with respect to dense crystalline polymorphs at ambient pressure, so volume collapse caused by compression at low temperature leads

to amorphization. A similar phenomenon is observed for H_2O –ice and semiconductor clathrate structures, as well as metal–organic framework (MOF) structures [25].

7 Configurational Energy Landscapes

As is the case for polyamorphism (Chapter 3.9), a convenient framework for interpreting the complex phenomenology surrounding PIA is provided by configurational energy landscape (CEL) models. These are constituted by a multidimensional plot of the potential energy (E) developed for all possible interparticle arrangements, defined by the bonding or other short- vs. long-range interactions between them. Each atomic arrangement constitutes a “configuration” that is typically represented schematically as a plot of energy vs. one or more of the generalized configurational coordinates. Between the deep, sharp minima representing ordered crystalline materials in the CEL occurs a “landscape” of amorphous configurations. As the pressure is varied, parts of the CEL change with respect to barrier heights. The relative positions of minima and pathways between these can be explored by thermal excitation, resulting in the variation of phase transition temperatures including melting, and the observation of metastable events such as PIA and polyamorphism. The CEL is affected by the extent of non-hydrostaticity of the field stress, including shear forces in different ways, and thus drives transformations that result in stabilization of new crystalline or amorphous polymorphs.

Two main scenarios are envisaged (Figure 4). In the first, the overall form of the CEL is assumed to remain

unchanged as the pressure increases, although the relative depth of potential minima and the barriers between them vary according to the relative density stabilization of different structural states. Pressurization at low temperature allows the crystal to be compressed metastably beyond its normal stability limit, until the $P\Delta V$ contribution to the energy allows the system to overcome local barriers and thus sample the surrounding configurational states. However, the thermal energy in the system is not sufficient to allow a suitable crystalline phase to nucleate and grow, so the resulting material is amorphous. In a second scenario, the topology of the CEL becomes modified during pressurization with the appearance, disappearance, or other modification of various minima and the barriers between them caused by mechanical, vibrational, or electronic instabilities, leading to collapse of the crystalline structure, but once more without permitting growth of a new crystalline phase.

Two critical factors govern the amorphization process: (i) the depth of the energy minima representing different crystalline states and (ii) the height of the energy barrier with respect to the amorphous megabasin, which can be increased by the number of defects (induced by doping, irradiation, etc.), surface/interface energy, strain, etc. Whenever this increase is sufficiently high, the initial crystal structure may be destabilized in favor of a new non-crystalline atomic configuration. Since the energy barrier between two crystalline phases that undergo reconstructive phase transformation is higher because of the need for bond-breaking and atomic diffusion events, amorphization may be easier to achieve under the low temperature and finite timescale conditions of the experiment.

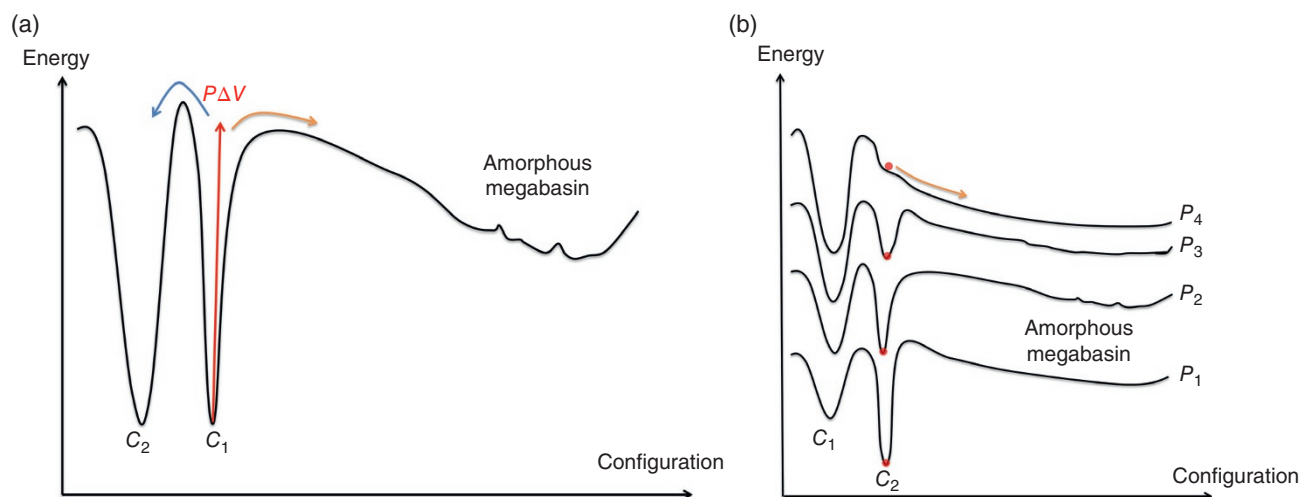


Figure 4 Two scenarios for understanding pressure effects within a configurational energy landscape (CEL) model. (a) If the CEL is not modified by pressure, the crystal can transform either to the thermodynamic stable crystal C_2 or to a metastable amorphous state depending on the manner in which its potential energy is increased by an energy term $P\Delta V$. (b) If the form of the CEL varies with pressure, instabilities leading to collapse of the crystal structure toward an amorphous state may appear.

8 Perspectives

The occurrence of PIA has raised fundamental questions about metastability and phase relationships in systems compressed or decompressed at low temperature. As a system is perturbed from its initial equilibrium state, any transition between stable phases associated with processes that involve energetic barriers or species diffusion becomes kinetically hindered, and the system can find itself trapped in a locus of structurally disordered metastable states. If the system is initially in a nonequilibrium amorphous state, it can be induced to cross a barrier into another “basin” of amorphous states with different density through the application of pressure, resulting in pressure-induced polyamorphism. Sampling of deep crystalline minima may also occur simultaneously with the PIA or polyamorphism phenomena, leading to technologically useful strategies for formation of novel nanocomposite materials containing intimate mixtures of crystalline and amorphous regions or inclusions. Continued studies and development of an understanding of PIA, LLPT, and polyamorphism are thus set to improve our deeper appreciation of the transformation properties of condensed matter in a highly metastable regime.

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3.11

Mechanical Properties of Inorganic Glasses

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1 Introduction

Network glasses, such as silicates, are brittle materials in which network-forming species form strong and directional, covalent metal–oxygen bonds whereas network-modifying species form relatively strong ionic oxygen–metal bonds. Owing to these strong bonds, the structures of network glasses are difficult to rearrange under applied stresses so that these materials are stiff, hard, and brittle. The moduli of glasses depend on composition, being related to both the atomic bonding and packing present in the glass. In the case of metallic glasses, where bonding is metallic rather than covalent-ionic, atomic packing is the dominant factor in determining moduli rather than bond strength. Along with toughness, hardness, and brittleness, elastic moduli are material properties whereas strength is a specimen property that depends on sample preparation and history.

In considering glasses as brittle materials, it is assumed that the temperature of interest is sufficiently below T_g that purely elastic deformation can be considered. Thus, high stresses result in fracture rather than causing plastic deformation. The only exception to this is high enough stresses arising from contact that can result in local permanent deformation as well as in the formation of cracks.

To account for these features, the following topics will be dealt with in this chapter: the importance of flaws in determining the strength of highly brittle solids such as glasses; elastic moduli of glasses, which are of fundamental interest in that they are, at least in principle, calculable from interatomic potentials; hardness and contact damage; the need to use statistics

when dealing with the strengths of brittle materials such as glasses; stress corrosion and subcritical crack growth; and finally potential methods for overcoming or reducing the effects of flaws to increase the practical strength of glass.

2 The Importance of Flaws

As brittle materials, glasses are sensitive to the presence of flaws. The importance of flaws in controlling the strength of silicate glasses was first recognized by Griffith [1] (Chapter 10.11). The basic problem is that flaws that control the strength of glass objects are introduced not only during most commercial glass-production processes, but also during use by contact, whether with sharp objects (modeled by Vicker's indentation, see Figure 1a) or rounded ones (modeled by Hertzian indentation, see Figure 1b). The nature of the damage is also affected by the degree of packing in the glass. Under Vicker's indentation in “normal” glasses (e.g. soda-lime-silica), a permanently deformed diamond-shaped region is created, with radial cracks emanating from its corners, whereas in “anomalous” glasses, such as pure silica that have low packing densities, the cracking tends to be circumferential as observed under Hertzian indentation. The difficulty of atomic rearrangement means that the hardnesses of glasses, measured from the size of the permanently deformed region under indentation, tend to be relatively high.

The sensitivity to flaws means that the strength of any particular glass object may change with time as a result of damage induced during usage. In addition, a set of nominally identical glass objects will not have a single well-defined value of strength so that strength data need to be treated statistically, with usually either a normal or a Weibull distribution. Furthermore, although the fracture

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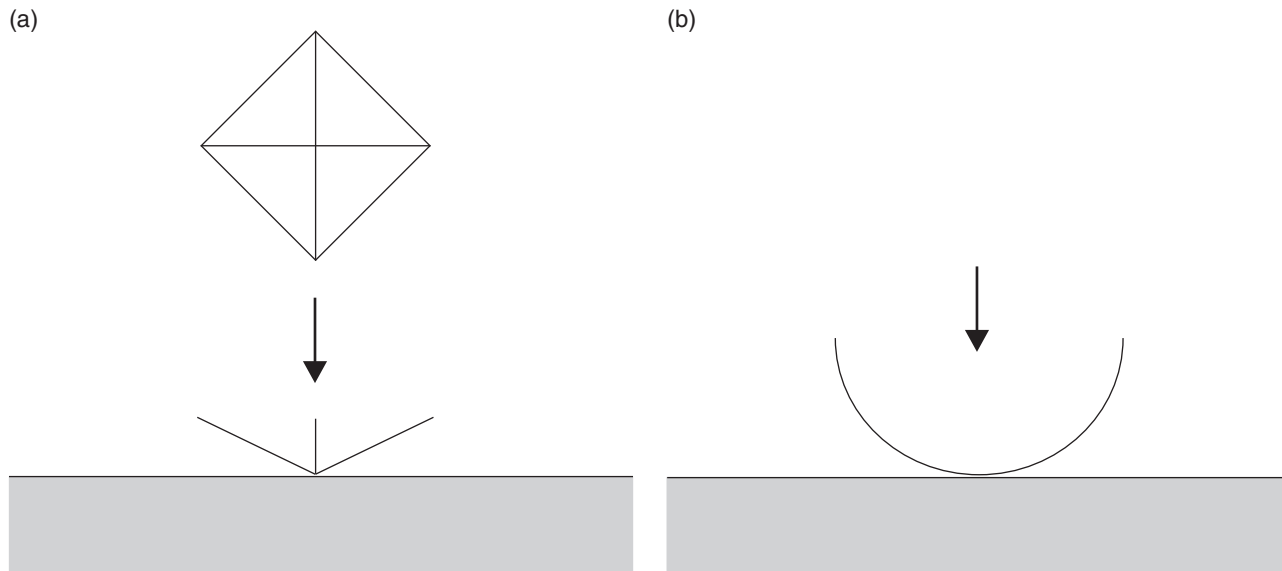


Figure 1 Schematic cross-sectional diagrams of indentation. (a) Vicker's, including a plan view of the indenter; (b) Hertzian.

of glass is usually perceived as sudden and catastrophic (brittle behavior), it was recognized as early as 1899 that loading of silicate glasses to failure at different loading rates gave different measured mean strengths. The reason is that subcritical crack growth can occur in stressed silicate glasses when atmospheric water is present, the rate of growth depending on humidity as shown by the classic data of Wiederhorn [2]. In recent times, water-induced subcritical crack growth has been a particular concern for predicting the lifetime of silica-fiber optic-telecommunication installations, although in reality, cable dig-up rate causes more failures than subcritical crack growth.

Coatings that fill flaws and are well bonded may be used to strengthen glasses (Chapter 8.2). Thick coatings are used to prevent damage in fiber optics whereas hot- and cold-end coatings on container glass are used during production to reduce frictional contacts and presumably to reduce contact damage. But a practical, transparent coating system providing both damage protection and strengthening by overcoming pre-existing flaws is currently not available.

A more widely used method of strengthening is to use compressive residual stresses, generated by thermal or chemical means and called thermally or chemically tempered glass, respectively (Chapter 3.12). The former is cheaper but is most effective with relatively simple geometries and requires reasonably thick glass. In comparison, chemical tempering is a much slower, more expensive process, but can achieve much greater levels of strengthening in a wider range of geometries including very thin glass, such as that used in mobile devices and modern display technologies.

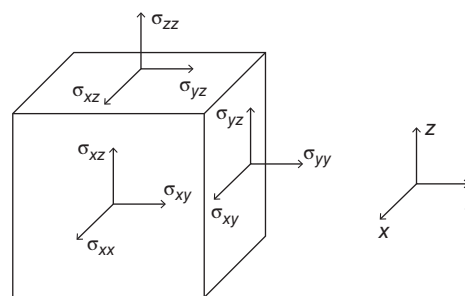


Figure 2 Stress components acting on a small element of a body.

3 Moduli and Hardness

3.1 Stress, Strain, and Elastic Moduli

When a balanced force is applied to any material, stresses and strains (deformations) are necessarily produced. A given force can be resolved into three components each parallel to the principal coordinate directions. Considering the projection of these components onto a small area oriented perpendicular to a principal coordinate direction and dividing by the area then gives rise to one normal stress and two shear stresses (see Figure 2). Repeating this procedure for all three coordinate directions gives rise to nine components of stress. Thus, a full description of stress and strain at a point requires nine components of stress, σ_{ij} and similarly nine components of strain, ϵ_{ij} . On symmetry grounds, one can show that only six components of stress are independent, namely the three normal stresses and three of the shear stresses. Similar arguments can be used to show that there are six

independent components of strain. Stresses and strains are related via the moduli of the material in question, which are in turn ultimately linked to the atomic bonds in the material. In the most general case, six independent components of stress need to be related to six independent components of strain meaning that 36 independent moduli are potentially required to describe the relationship between stress and strain in a small region of material. However, as glasses are (usually) isotropic materials, only two independent moduli are required. These moduli can be any pair of Young's modulus (E), shear modulus (G_s), bulk modulus (B), and Poisson's ratio (ν). Once any pair has been obtained, the other moduli can be obtained via

$$E = 3B(1 + \nu), \quad (1)$$

$$G_s = \frac{E}{2(1 + \nu)}, \quad (2)$$

or related equations. The macroscopic moduli are related to stiffnesses and strengths of the underlying atomic bonds (two parameters that are usually proportional to each other and will thus be used interchangeably although they are not synonymous). As such, correlations between glass composition and the moduli of different glasses are expected and indeed are observed [3]. This relationship is not completely straightforward as atomic packing, which reflects the bond orientation, arrangement, and connectivity, also has an effect on the moduli of glasses; Poisson's ratio, for instance, essentially increases with packing fraction (see Figure 3), albeit in a nonlinear fashion, from pure silica to metallic glasses [3]. It is notable that many network glasses have similar packing densities, but different Poisson's ratios, hence Figure 3 shows a sharp increase in Poisson's ratio at a packing fraction of about 0.5. This indicates that varying bond strengths dominate the observed behavior in this region rather than the packing fraction, which is different from the monotonic trend predicted by the earlier model of Makashima and Mackenzie [4]. There is also a tendency for moduli to increase with the glass transition temperature, T_g (Figure 4; based on data from [5]), not because of a direct relationship, but because both moduli and T_g are related to the underlying bond strengths.

Typically, a small reduction in Young's modulus and shear modulus is seen as temperatures increase, a significant reduction being observed as the glass changes from an elastic solid as T_g is approached. Notably, pure silica, which is an anomalous glass, exhibits an increase in

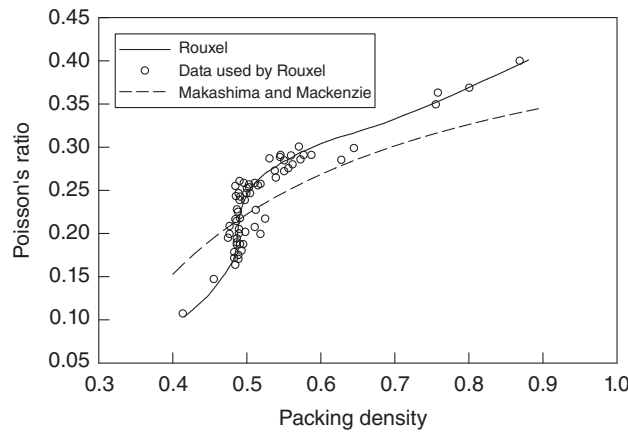


Figure 3 Schematic plot showing the relationship between Poisson's ratio and packing fraction found by Rouxel (Source: Data from [3]) and the predictive model of Makashima and Mackenzie [4].

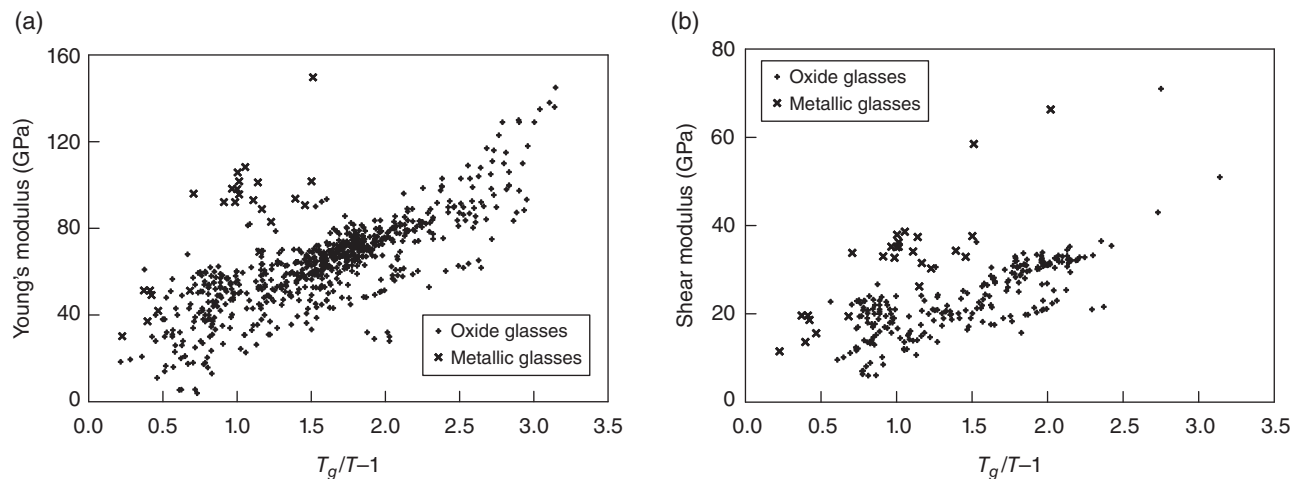


Figure 4 Effect of temperature on elastic moduli. (a) Young's and (b) shear moduli versus normalized T_g for a range of oxide and metallic glasses. Source: Data extracted from the SciGlass database [5].

Young's modulus and shear modulus with increasing temperature.

3.2 Hardness and Plasticity

The difficulty of atomic rearrangement means that glasses tend to have high yield strengths and thus hardnesses, the hardness scaling with Young's modulus. Such high hardness values mean that, if subjected to indentation by a Vicker's diamond indenter, many glasses will be deformed in only a small volume. The presence of actual deformation does, however, demonstrate that glasses are *not* ideally brittle materials at room temperature. At sufficiently high temperatures, viscoelasticity will also occur with a concomitant reduction in measured hardness when T_g is being approached.

The nature of the deformed region under a room-temperature indentation changes quite markedly with atomic packing density. In this context, "normal" glasses, including soda-lime-silica, have a high packing density and show a diamond-shaped, permanent indentation, arising primarily from shear flow, with median-radial cracks emanating from its corners (Figure 5a). The median-radial cracks have been widely used to obtain comparative fracture toughness measurements (see, for example, [6, 7]), although the validity of this approach is now being widely questioned and may give contradictory trends when compared to more conventional procedures for measuring fracture toughness [8, 9].

"Anomalous" glasses, including pure silica, have low packing densities so that they much more readily experience densification under the indenter; for pure silica, 80% of the deformation actually arises from shear flow [10]. This gives rise to more circular crack patterns (compared to what is seen in "normal" glasses) around the indentation site with little or no radial cracking (see Figure 5b). The occurrence of both densification and shear flow in pure silica glass explains why pure silica glass has a lower hardness than its crystalline counterpart quartz, where only shear flow occurs under indentation. It is notable that the hardness of pure silica glass that has already been densified under high pressure significantly increases toward the crystalline values as deformation through shear flow becomes the only available mechanism [9].

Based on the dependence of the indentation stress field on Poisson's ratio, Rouxel and coworkers [8, 11] have recently categorized glasses as resilient ($0.10 \leq \nu \leq 0.20$), semi-resilient ($0.20 \leq \nu \leq 0.25$), easily damaged ($0.25 \leq \nu \leq 0.33$), or highly resilient ($0.33 < \nu$) reflecting how readily cracks can be generated around an indentation.

Recent work on ternary borate glasses [12] has demonstrated that in principle one may calculate hardness by considering the bonding constraints present in the glass. This constraint theory approach has previously been applied to chalcogenide glasses (Chapter 2.7). In some binary chalcogenide systems, a maximum in toughness and minimum in brittleness is observed around the rigidity threshold. Despite the correlations observed by Rouxel

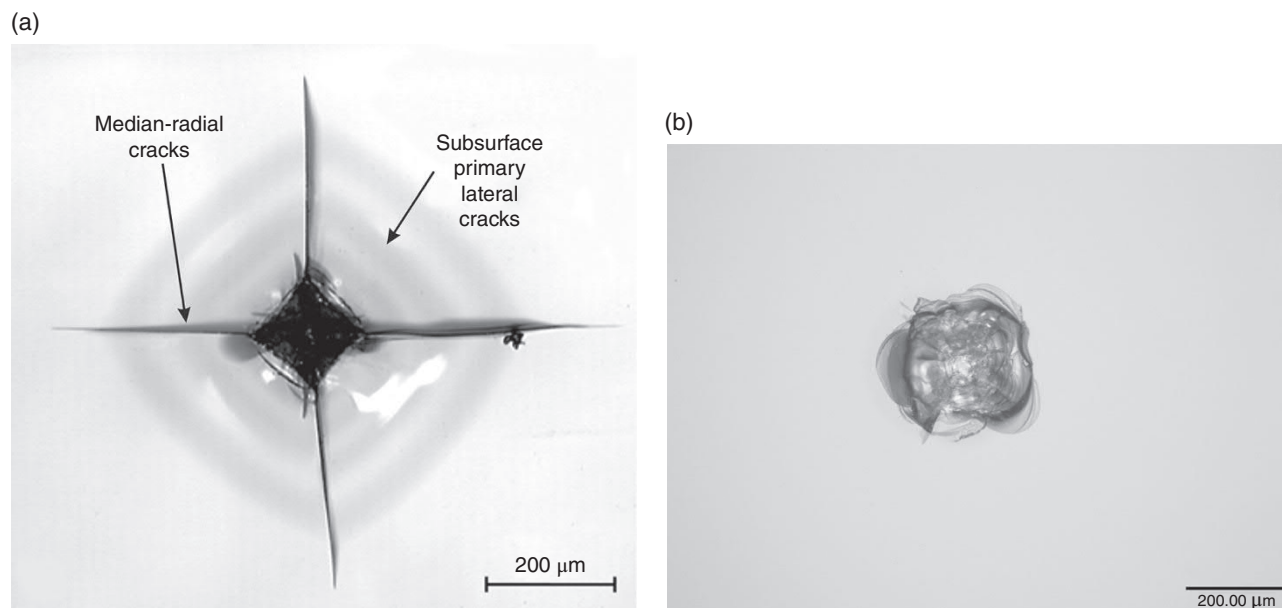


Figure 5 Contrast between Vicker's indentations on "normal" and "anomalous" glasses. (a) Soda-lime-silica glass showing the centrally deformed region, cross-shaped median-radial cracks as well as primary subsurface lateral cracks, which are visible as interference fringes; (b) fused silica.

and coworkers [8, 11] or the work of Smedsjkaer et al. [12], however, the fact remains that there is no overall theory that predicts the variation of the mechanical properties of glass with composition.

4 Fracture Toughness and Strength

Arguments based on the energy required to break an individual bond can be used to show that the theoretical strength, σ_{th} , of any material should be a significant fraction of the Young's modulus of that material. The simplest version of these arguments assumes a sinusoidal approximation for the interatomic force–displacement curve and equates the area under the force–displacement curve with the surface energy, γ , of the new crack surfaces. This gives

$$\sigma_{th} = \sqrt{\frac{E\gamma}{a_0}}, \quad (3)$$

where a_0 is the interatomic distance. For soda-lime-silica ($E \approx 70$ GPa, $\gamma \approx 3.5$ J/m², and $a_0 \approx 0.3$ nm) Eq. (3) gives $\sigma_{th} = 29$ GPa $\approx \frac{E}{2.5}$. More complex models indicate that in general $\frac{E}{10} \leq \sigma_{th} \leq \frac{E}{5}$. In practice, however, the strengths of materials are usually significantly less than these theoretical values; in the case of bulk network glasses, practical strengths are of the order of $\frac{E}{1000}$. This is due to the presence of strength-controlling flaws or cracks, which are often referred to as Griffith flaws, although the precise nature of these flaws, and whether they have any relationship to the underlying glass structure [13] is still a matter for debate.

As glasses do not have a regular crystalline structure or grain structure, once a crack starts propagating, its

direction of growth is perpendicular to that of local principal tension rather than following microstructural features in the glass. Initially, this leads to distinctively smooth fracture surfaces that may be gently curved depending on the particular local stress field ahead of the growing crack (Figure 6). This type of fracture is referred to as *conchoidal*. Once a crack interacts with reflected stress waves, Wallner lines may be generated on the fracture surface. Alternatively, if the crack reaches its terminal velocity and starts to bifurcate, then features variously known as hackle or river lines may be generated (Figure 6).

Inspection of fracture surfaces shows that usually the strength-controlling defects are present in the original surface of the glass component. For a flaw of depth, a , oriented perpendicularly to an applied stress, σ_{app} , the ij th component of stress, σ_{ij} , at the crack tip is given by

$$\sigma_{ij} = \frac{C\sigma_{app}\sqrt{\pi a}}{\sqrt{2\pi r}} f_{ij}(\theta), \quad (4)$$

where r is the distance from the crack tip and f_{ij} is a function of θ , the angular distance from the line of the crack. The numerator of Eq. (4) may be written as

$$K_I = C\sigma_{app}\sqrt{\pi a}, \quad (5)$$

where K_I is known as the mode I stress-intensity factor. In general, C in Eqs. (4) and (5) is a function of crack length. For small surface cracks, such as those typically controlling the strength of glasses, it can be approximated as a short through-edge crack in which case $C \approx 1.12$. Although a through-edge crack is clearly a major simplification (see Figure 7) compared to real crack geometries, then this approximation gives reasonable insight for surface cracks in glasses if $a \ll W$.



Figure 6 The smooth curved surfaces associated with conchoidal fracture and river lines in an obsidian sample.

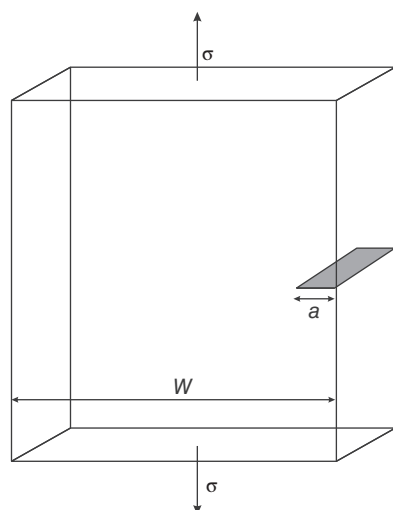


Figure 7 Schematic diagram of a through-edge crack.

Fracture occurs when

$$K_I \geq K_{Ic}, \quad (6)$$

where K_{Ic} is known as the critical stress-intensity factor which, in the absence of residual stresses, is equal to the fracture toughness, the measure of resistance to crack growth of a material. As a result, K_{Ic} is usually also referred to as the fracture toughness of the material. If residual stresses are present, however, it is better to differentiate between the critical stress intensity for fracture, which is related to the stresses present as well as the loading geometry, and the fracture toughness, which is a material property. Thus, in the following, K_{Ic} will be used for the critical stress-intensity factor for fracture and T for

the fracture toughness, i.e. if no residual stresses are present, then

$$K_I \geq K_{Ic} = T. \quad (7)$$

If residual stresses are present, then the condition for fracture, Eq. (7), becomes

$$K_I \geq K_{Ic} = T + K_{rs}, \quad (8)$$

where K_{rs} is the stress-intensity factor due to the residual stresses. For surface flaws restricted to the compressive stress region of thermally or chemically tempered glass, $K_{rs} > 0$, so that the critical stress-intensity factor at failure is greater than the intrinsic resistance to crack growth (in other cases, K_{rs} may be positive or negative). As a result, such glasses are sometimes, albeit incorrectly, referred to as toughened glasses; in practice, the underlying resistance to crack growth, i.e. the strength of the bonds in such glasses is essentially unchanged.

Glasses are often viewed as archetypal brittle materials because their fracture toughness is generally very low even in comparison with other brittle materials. Some typical values are given in Table 1. The ratio of hardness to fracture toughness, usually calculated from indentation approaches, has been labeled brittleness and suggested to scale with density for “normal” silicate glasses [14] although more recent studies have questioned this relationship [15].

The derivation of Eq. (4) assumes that cracks are infinitely sharp and that the stress becomes infinite at their tip ($r = 0$). In practice, this cannot be the case and some yielding will occur instead ahead of the crack tip. Owing to the difficulty of bond rearrangement in network glasses, which causes them to have very high yield

Table 1 Representative mechanical property ranges for different glass families.

Glass composition	E (GPa)	μ	$\frac{E}{1-\nu^2}$ (GPa)	Hardness (GPa)	Fracture toughness (MPa m ^{1/2})	Brittleness (μm ^{-1/2})
Soda-lime-silica	70–75	0.22–0.25	74–80	5.4–6.6	0.72–0.82	6.5–9
Silica	72	0.17	74	7.0–7.5	0.74–0.81	8.6–10
E-glass (borosilicate)	72.3				0.8–0.9	
Nuclear waste borosilicate (modified R7T7)			78	6.8		8
Aluminosilicate	83–91			5.4–5.9	0.85–0.96	5.6–6.9
Soda-lime-borate	49–73	0.27	53–79	3.6–5.0	0.82–1.0	3.6–6.1
Iron phosphate	70–73	0.24–0.25	74–77	3.2	0.95	3.4
ZBLAN	51–55	0.30–0.31	56–59	1.9		
Ge–Sb–Se	14–23	0.25–0.30		0.5–2.0	0.2–0.3	8–14
Zr-based metallic glasses	75–105	0.33–0.38	85–120		20–85	

Source: Data from various sources; a fuller range of moduli data can be found in [3].

strengths, yielding occurs over a very small volume of material on the scale of a few interatomic distances at most. The very localized nature of such yielding means that this process does not significantly contribute to the resistance to fracture and, as a result, that the fracture toughness is very low. Hence the stress–strain curve of network glasses under tensile or bending loading is essentially linear until failure, which is usually sudden and catastrophic. As noted above, under compressive indentation loading, permanent deformation can occur.

5 Flaws and Strength

5.1 Flaw Sizes

The flaw sensitivity of glasses means that they are susceptible to damage by contact either with another glass component or with another materials; such contacts naturally arise during current production of most bulk glass. Other processes, such as the removal of the indented side regions (seldge removal) of a float glass ribbon, can also introduce damage and various distinct flaw types can be identified on the edges of float glass (Chapter 1.4). Once bulk glass is in use, post-manufacture, further contact damage can and does arise. Thus, the strength of bulk glass, even by the end of the production process, is much less than the theoretical value and will often be further reduced by damage occurring during use. Typical flaw sizes in as-manufactured glass are calculated with Eq. (5) and $C = 1.12$ to determine when the stress-intensity factor becomes equal to the fracture toughness, to be of the order of a few tens of microns in depth. In comparison, downdrawn silica-fiber optics are prepared with a fresh outer surface that is coated immediately after forming to protect the surface from subsequent contact damage (Chapter 6.4). In this case, flaw sizes are calculated to be on a nanometric scale. As a result, the strengths of such fibers are very high, especially if measured under liquid nitrogen or liquid helium so that stress corrosion (see Section 5) during testing is suppressed. The high strengths of silica-fiber optics are essentially maintained over time, thanks to the prevention of contact damage, although a limited degradation in strength called “zero stress aging” is observed, which arises from a roughening of the glass surface by water that diffuses through the protective coating.

As noted above, the typical size of surface flaws in bulk glasses is of the order of a few tens of micrometers. Although flaws of this size could, in principle, be visible prior to fracture, in practice they are generally not, suggesting that the strength-controlling surface defects in bulk glasses are tightly closed and thus not resolvable optically. Obviously, gross defects can be seen but,

depending on their position and loading geometry, these may or may not actually be the strength-controlling defect in a particular glass object.

Applying Eq. (5) to the strength of silica-fiber optics tested under liquid nitrogen gives a defect size similar to the size a SiO_4 tetrahedron. However, this value needs to be treated with caution in that the derivation of Eqs. (4) and (5) assumes that materials are continua, i.e. it ignores the existence of atomic-level structure despite the fact that the discontinuity of matter should be considered in describing phenomena at this scale. Given that the observed variation in the strength of these fibers can be accounted for by the variation in their diameter, the calculation does suggest that the strength-controlling features in silica-fiber optics are related to something intrinsic in the glass structure rather than to an externally imposed damage site. More generally, the strengths of glasses measured by testing of newly drawn fibers under liquid nitrogen, such that water attack is suppressed, have therefore been defined as intrinsic by Kurkjian et al. [16]. In this case, it has been found that the melt temperature and soak time before drawing affect the intrinsic strength [17], again suggesting that the strength-controlling features are related to features in the glass/melt structure such as alkali channels [13] although the actual cause of this effect is unclear. In most practical applications of bulk glass, however, strengths dominated by extrinsic flaws are the norm.

It should be noted that, even under ambient conditions, the strength of most glass fibers is significantly larger than that of the bulk glass of the same composition. This difference can be ascribed to the presence of smaller extrinsic defects in fibers than in bulk glasses, since large defects that can be present in bulk glass would simply result in a broken fiber, as well as possibly to the higher fictive temperature of fibers caused by the rapid cooling experienced during fiber production [17]. In addition, the degree of structural anisotropy caused by the drawing stress influences the measured fiber strength [18]. The presence of coatings that prevent or minimize surface damage thus enable these high fiber strengths to be maintained over time.

Although rapid cooling seems to aid fiber strength, the large gradients in temperature generated during cooling and, hence, of residual stress that would then be generated in bulk products would normally result in spontaneous fracture (unless carefully controlled to produce thermally tempered glass). Thus, bulk glass articles are annealed to avoid the formation of undesirable residual stresses that can cause spontaneous fracture. As cooling times essentially scale as the square of the section thickness, the annealing process for thicker sections is necessarily very long and expensive.

One particular area where cracking is potentially of concern is in vitrified nuclear waste. In a heat-generating wasteform, such as those produced by vitrification of high-level reprocessing wastes in the United Kingdom and France, significant self-heating from the intense radiation field probably mitigate, to some extent, against this cracking which has been directly observed on more rapidly cooled “inactive” simulant wasteforms. In addition, radiation damage will arise through radioactive decay. Although it is not clear what effect such damage will have on glass strength, it is probable that the size of these radiation-induced defects is insignificant compared to that of the cracks arising from temperature gradients on cooling. In practice, the vitrified nuclear wastes are contained in stainless-steel canisters, which provide mechanical integrity for handling so that cracking primarily affects the amount of surface potentially available for chemical attack.

5.2 Flaw Statistics

As the flaws generated by contact and other damage mechanisms are necessarily variable, the strengths of a set of nominally identical pieces of glass will also be variable and a statistical treatment will have to be applied to any glass strength data. The most commonly used treatments assume that the measured strengths follow either a normal or a Weibull distribution. The symmetric, normal distribution is characterized by two parameters, namely the mean, $\bar{\sigma}$, and the standard deviation, s , which can be readily evaluated with a scientific calculator or spreadsheet. Compared to the normal distribution, the Weibull distribution is arguably preferable in that it gives a greater emphasis to the low strength tail that is especially relevant from a practical standpoint. With limited datasets, however, there is unlikely to be sufficient evidence to favor either of these distributions over the other.

For the Weibull distribution, the basic analysis is a little more complicated and either two or three parameters may be used to characterize the distribution. The three-parameter Weibull distribution states that the risk of failure, F , is given by

$$F = 1 - \exp \left[- \left(\frac{\sigma - \sigma_u}{\sigma_0^*} \right)^m \right], \quad (9)$$

where σ_0^* is a characteristic strength (which, similarly to the mean in the normal distribution, is a measure of the position of the peak of the distribution); m is the Weibull modulus, which is a measure of the width of the distribution (with a large value of m indicating a narrow spread of strength values); and σ_u is the stress below which the probability of failure is zero. In practice,

because it is difficult to evaluate σ_u in a straightforward fashion, the two-parameter distribution

$$F = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0^*} \right)^m \right] \quad (10)$$

is often used instead of Eq. (9). The two-parameter distribution is intrinsically more conservative; however, its use may not be appropriate in all situations. Application of Eq. (10) instead of Eq. (9) is, for instance, particularly problematic when assessing the strengths of reinforcing fibers selected from a fiber tow [19]. In both Eqs. (9) and (10), the normalizing characteristic strength term is related to the loading geometry and the volume, V , or surface area, S , or for fibers length, L , of stressed material by $\sigma_0^* = \sigma_0 (L_f V)^{-1/m}$, $\sigma_0^* = \sigma_0 (L_f A)^{-1/m}$, or $\sigma_0^* = \sigma_0 (L_f L)^{-1/m}$, respectively, where L_f is a dimensionless geometry-dependent loading factor (1 for straight pull tension and a function of m for other geometries) and σ_0 is another normalizing term without obvious physical meaning due to its unusual dimensions (e.g. MPa m^{3/m} for the volume case). Use of the loading factors and σ_0 is only necessary if one tries to relate data from one sample geometry/size to another, a situation that will not be considered further here.

By taking logs twice, one can rearrange Eq. (10) into the form of a straight line

$$\ln [-\ln (1 - F)] = m \ln (\sigma) - m \ln (\sigma_0^*), \quad (11)$$

which provides a basis for evaluating the Weibull modulus. Thus, for a given set of data, one obtains the risk of failure, F , by ranking the strength values in ascending order and assigning each value a rank, r , duplicate values being assigned different adjacent ranks. The risk of failure may then be estimated with

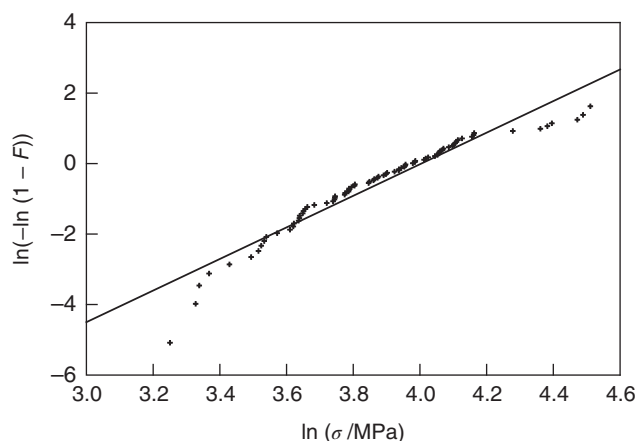


Figure 8 Example of a Weibull plot, where σ is the measured strength and F is the estimated risk of failure. Source: Data from four-point edge strength measurements on float-glass samples.

$$F = \frac{r - 0.5}{N}, \quad (12)$$

where N is the total number of samples. Other similar estimators of F can be used instead of Eq. (12). A plot of $\ln[-\ln(1 - F)]$ versus $\ln(\sigma)$ ideally will yield a straight line the slope of which is the Weibull modulus and the intercept with the y -axis enables evaluation of σ_0^* . For the example Weibull plot shown in Figure 8, the Weibull modulus is 4.5 with an intercept value of -17.94 , hence $\sigma_0^* = 53.9$ MPa. Deviations from a straight line in the tails of the distribution (as seen in Figure 8) tend to reflect insufficient numbers of samples being tested; such deviations elsewhere in the plot may also suggest that more than one flaw type may be causing failure. One can rectify the former by increasing the numbers of samples tested whereas the presence of more than one flaw type requires more complex analysis to separate out the different flaw distributions.

For sample sets with a narrow distribution of strength values, the Weibull modulus will be high – being of the order 50 for freshly drawn silica fibers, whereas for most glasses it will typically be between 2 and 10, indicating a broad distribution of strength values.

The practical problem with any statistical distribution of strengths is that the distribution measured on a new set of glass articles, or laboratory samples, is not necessarily representative of components that have been in use for some time. Proof testing in which all components are subjected to a certain stress level, which ensures that all components can survive this particular minimum stress level obviously can guarantee this performance only before subsequent handling and use. Unless carried out in an inert environment, such testing may actually compromise the strength of the articles before use, if stress corrosion then takes place during the proof test (see Section 5).

6 Chemically Assisted Crack Growth – Stress Corrosion

Fundamentally, fracture involves the breaking of chemical bonds. Thus, direct chemical attack on stressed bonds can result in crack growth, in a similar fashion to sufficiently high applied stresses; the significant difference is that the chemically assisted crack growth is usually very slow, with velocities lower than 1 mm/s; for comparison, the fast fracture normally experienced when a soda-lime-silica glass is broken reaches 1.5 km/s. The slow crack-growth process is referred to as subcritical crack growth and the process causing it is referred to as *stress corrosion*,

a term to be preferred over *static fatigue* because fatigue actually implies cyclical loading.

In silicate glasses, such chemically mediated crack growth can occur in the presence of atmospheric water. The reason is that strained $-\text{Si}-\text{O}-\text{Si}-$ bonds are more susceptible to nucleophilic attack by water, which breaks the linkage between adjacent silica tetrahedra by giving two disconnected $-\text{Si}-\text{OH}$ groups that relieve the local strain (Chapter 5.11). Strained $-\text{Si}-\text{O}-\text{Si}-$ bonds are present at any crack tip that is under some level of applied stress and will also be present in rings that contain fewer than six silica tetrahedra. The rate of crack growth as a function of the applied stress-intensity factor is shown schematically in Figure 9 where it appears that there is a certain minimum stress intensity level, K_{Ith} below which cracks do not grow. The presence of this threshold intensity factor for stress corrosion is subject to some debate. A number of different experimental techniques have been developed to measure K_{Ith} , which do not always give consistent results; typically, the values of K_{Ith} are between 25 and 33% of the fracture toughness. Above the threshold region, the crack growth velocity arising from direct chemical attack depends on the applied stress-intensity factor (Figure 9, region I). As suggested by Eq. (5) for a given applied stress, the stress-intensity factor at a crack tip usually increases with the crack length, hence the crack velocity also increases. Eventually, the crack becomes sufficiently long that the rate of chemical attack is limited by diffusion of water to the strained bonds at the crack tip so that the crack velocity reaches a plateau (Figure 9, region II). Finally, the crack becomes so long that the applied stress-intensity factor becomes equal to the fracture toughness: the transition to fast fracture occurs, the crack then rapidly accelerating to its terminal velocity (Figure 9, region III). Additional phenomena such as alkali diffusion under the local stress gradients around the crack tip may also occur around the growing crack tip, further affecting the stress corrosion chemistry [20].

In the literature, either an exponential function is fitted to the crack velocity data in region I

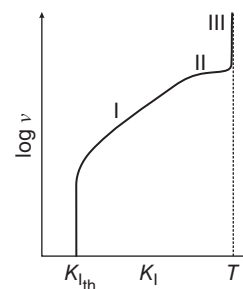


Figure 9 Schematic diagram of subcritical crack growth rate versus applied stress-intensity factor for silicate glasses.

$$\nu = \frac{da}{dt} = A \exp \left(n \frac{K_I}{K_{Ic}} \right), \quad (13)$$

implying the log-linear plot exemplified in Figure 9; or a power-law function is fitted

$$\nu = \frac{da}{dt} = A_p K_I^{n_p}, \quad (14)$$

implying that Figure 9 should be a log-log plot. In Eqs. (13) and (14), A , A_p , n , and n_p are empirical constants, although in principle both A and A_p should be related to the relative humidity and to an activation energy. In Eq. (14), n_p is found experimentally to take typical values between 15 and 50 depending on composition. In principle, Eq. (13) should be preferred as its parameters lend themselves to clearer physical interpretation [19, 21]. However, Eq. (13) lacks a closed-form solution for the commonly used conditions of constant stress-rate test so that Eq. (14) is often used instead. We will now assume that the critical crack length for failure is much greater than the initial crack length. For a constant stress-rate test at a loading rate, $\dot{\sigma}$, Eq. (14) then predicts that the mean failure stress, $\bar{\sigma}_f$, is given by

$$\bar{\sigma}_f^{n+1} = \frac{2\dot{\sigma}\bar{\sigma}_{\text{inert}}^{n_p-2}(n_p+1)}{A_p C^2 \pi K_{Ic}^{n_p-2}(n_p-2)}, \quad (15)$$

where $\bar{\sigma}_{\text{inert}}$ is the mean strength measured under inert conditions. In other words, Eq. (15) indicates that a log-log plot of $\bar{\sigma}_f$ versus stress rate should be a straight line with a positive slope. Although more convenient for constant-stress test methods, Eq. (14) tends to give overly optimistic results compared to Eq. (13) when used for extrapolated lifetime predictions.

7 Improving the Practical Strength of Glass

7.1 Residual Stresses – Thermal and Chemical Tempering

Increasing the practical strengths of bulk glasses is widely seen as desirable as it should, in particular, allow the production of lighter weight glass articles and, thus, lower production costs. One can achieve improved glass strengths by inducing compressive surface stresses so that K_{rs} in Eq. (8) is positive or by some types of surface coating that either prevent flaw formation or overcome pre-existing flaws.

Surface compressive residual stresses may be induced in glasses by two primary means – thermal and chemical tempering (Chapter 3.12). In thermal tempering, the glass is heated above T_g and then rapidly cooled, commonly by jets of air. This process can achieve maximum surface compressive stresses (σ_c) of the order of 100 MPa and can only be usefully applied to relatively simple geometries. Thermal tempering has therefore found its major use in the flat-glass industry, although it was originally discovered in the production of the rounded Prince Rupert drops (Chapter 10.11) and is also used on some glassware. Although the exterior of thermally tempered glass is under compression, the interior is necessarily under compensating tension with the maximum tensile stress being of the order of $\sigma_c/2$; the stress distribution is often taken to be parabolic through the glass thickness (see Figure 10a). For a parabolic stress distribution, the compressive layer depth is ~21% of the glass thickness, t , the compressive stress acting over a typical surface crack may be taken as being approximately constant and hence the residual stress term in Eq. (8) is given by

$$K_{rs} = 1.12\sigma_c\sqrt{\pi a}. \quad (16)$$

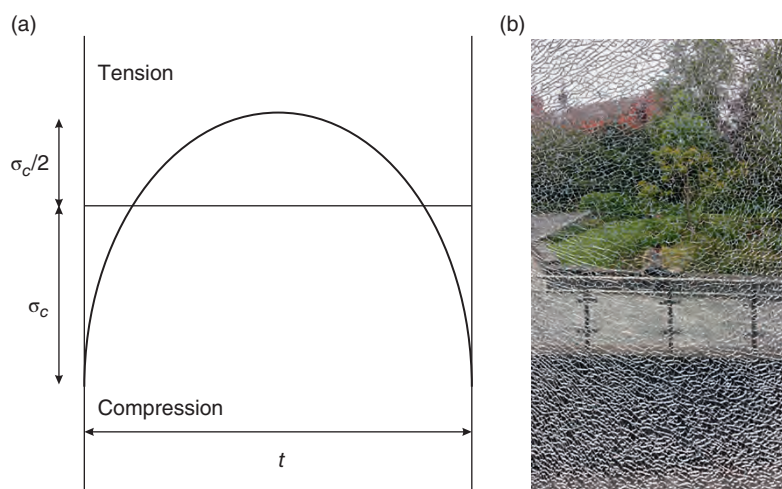


Figure 10 Thermally tempered glass. (a) Parabolic thermal tempering stress distribution; (b) typical fracture pattern.

As a result of the high interior tensile stresses, a crack that begins to grow and penetrates the interior has so much excess energy that it bifurcates many times to produce characteristic small fragments (see Figure 10b). These characteristic small fragments pose a significantly lower risk of severe injury than the large shards typically produced during the fracture of annealed glass, which is why thermally tempered glass is also known as safety glass. The high interior tensile stresses in thermally tempered glasses can also lead to failure from an interior defect if nickel sulfide or other inclusions are present in the glass (Chapter 3.12).

Chemical tempering involves thermally assisted ion exchange of a smaller ion by a larger one in a molten salt bath at a temperature below T_g to minimize stress relaxation during the process (Chapter 3.12). Most commonly, sodium ions in the surface of the glass are replaced by potassium ions. As a diffusion-based process chemical tempering is much slower, and more expensive, than thermal tempering, but yields much greater surface compressive stress levels, over a (case) depth of tens to a few hundreds of microns and thus very high degrees of strengthening. In this case, the residual stress distribution varies rapidly with depth so that calculation of the residual stress term in Eq. (8) has to take this effect into account. Glass compositions can be selected to optimize the ion exchange process, which has the additional advantage of being applicable to very thin glass. As a result, chemical tempering is now widely used to produce thin display glass with a very high-strength.

7.2 Coatings

Coatings applied to the surface of glass can have beneficial effects on mechanical properties (Chapters 6.7 and 8.1). Practical coatings essentially fall into two types – those that help prevent damage and those that overcome pre-existing damage. The former include the two-layer acrylate coatings that are applied to newly drawn silica-fiber optics as well as the hot- and cold-end coating combinations applied during container glass production (Chapter 6.4). Coatings that overcome pre-existing damage are flaw filling and include sol–gel and epoxy-based systems. The acrylate coatings on fiber optics are thick enough to prevent contact damage (softer coatings have to be relatively thick to sufficiently reduce the effect of contact stresses [22]), while hot- and cold-end coating systems increase the lubricity of the glass surface thereby reducing the extent of subsequent contact damage but not preventing it (and not overcoming any contact damage arising from earlier in the production process).

Sol–gel-derived silica and epoxy-based coatings have been demonstrated to overcome pre-existing damage in glass. These strengthening coatings must have low

enough viscosities on application to penetrate flaws and they also need to develop a good chemical bond with the glass. For an epoxy-based system, Hand et al. [23] showed that residual stresses developed, because of thermal expansion mismatch, inside a well-bonded coating penetrating pre-existing defects could explain the improved strength of the coated glass. For solvent- and water-based coating systems, these stresses were calculated to be about 35 and 90 MPa, respectively. More recently, Briard et al. [24] have attributed a similar level of closure stresses in an organosilane coating system to the elastic response of the material bridging the crack. Much of the work on demonstrating strengthening coatings has been conducted on glass samples containing relatively large, deliberately introduced, controlled defects. It is therefore notable that the recovered strengths remain well below the theoretical values, implying that only larger flaws are successfully penetrated by the coatings [25], which is not entirely surprising given that strength-controlling defects are often not optically resolvable. In addition, the application conditions needed for flaw penetration means that such strengthening coatings tend to be too thin to prevent subsequent contact damage [22].

8 Perspectives

Glasses are brittle, flaw-sensitive materials that under normal conditions achieve strengths that are only a small fraction of their theoretical values. Preventing contact damage during production, as is the case with the drawing of fiber optics from a preform (Chapter 6.4) and the Corning fusion overflow process for flat glass production (Chapter 1.4), combined with suitable coatings or ion exchange can be and is used to achieve high practical strengths for high-value end applications. Thermal tempering may be used to increase strength (and safety) for some window applications, although in others laminated systems are preferred. The stiffness associated with the relatively thick sections of conventional glass windows is often utilized from a structural design perspective (Chapter 9.1), but adds significant weight in transport applications whereas users are looking at ways of significantly reducing weight. Weight reduction is also a significant concern for containers and glassware, where glass is competing with polymers, and thus economic methods of achieving consistently high strengths for these applications are still being sought. Although the mechanical properties of glasses vary with composition [3, 12, 14, 15], compositional modifications on their own are only likely to produce limited benefits. If they can be used to optimize other processes such as ion exchange, however, then more substantial gains in mechanical properties are

achievable. Thus, at the time of writing, the fundamental challenge for the bulk glass industry (and thus a major challenge for glass research) is to find a way of producing consistently stronger glass products with a high Weibull modulus, enabling thinner glassware, containers, and windows, while keeping costs down to a manageable level.

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3.12

Strengthening of Oxide Glasses

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1 Introduction

Most oxide glasses are weak in bending and tension as compared to many other materials. Their strength can nonetheless be increased through various routes. Strengthening of glass is alternatively called toughening, tempering, or hardening. While nowadays widely employed technologically, it remains an important topic also on research and fundamental levels as glass keeps finding new applications for which improved mechanical properties are needed either directly or indirectly, i.e. to reduce the amount of material used and, thus, to lower weight. In this way, one can reduce CO₂ emissions, save fabrication costs, lower transportation expenses (which are particularly important for architectural application), and make handling of glass products easier. As discussed in Chapter 3.11, the practical strength of glass is only a small fraction of the theoretical limit because fracture always starts from flaws that are inevitably produced at the surface during fabrication or use. Varying widely, the severity of these defects depends to a large extent on the effective surface area and also on postproduction treatments of the glass products. When a glass sheet is mechanically cut, it is, for example, severely damaged by edge surface defects.

Increasing the strength of glass is currently achieved in three general ways, namely, (i) elimination or neutralization of existing flaws; (ii) prevention of flaw formation; and (iii) improvement of the strength of glass, which contains surface flaws, by introducing residual surface compressive stresses (see Figure 1). Typical examples of the first kind are the various polishing techniques used to

smooth the surface, e.g. chemical-mechanical polishing (CMP), etching (chemical), fire/flame, laser, and fluid-jet polishing. The second group includes most types of coatings, such as sol–gel or epoxy products whose purpose is to protect the glass surface. Because coatings partially can fill surface defects, they are in addition an example of the third kind of processes that mainly comprises thermal and chemical strengthening.

In the present chapter, these methods will be successively described, the basic principles of fracture being described in Chapter 3.11 on mechanical properties. As a convenient starting point, the main features of thermal and chemical strengthening are summarized in Table 1 whereas their strengthening characteristics are listed in Table 2 for soda-lime-silicate glass used in buildings. There are of course cases where combinations of different methods have been used, but such combinations have not received widespread commercial attention yet. As briefly stated at the end of this chapter, there is also a fourth group; it aims at improving the intrinsic strength of glass through a control of its structural anisotropy.

2 Strength and Stresses

The practical (or usable) strength of oxide glasses [2] is an extrinsic property, i.e. it depends to a lesser extent on glass composition than it does on the surface characteristics and geometry. Because it also varies from one glass piece to another, one is advised to evaluate glass strength by performing a number of rupture tests and make fits to the data with a normal or Weibull statistical distribution (Chapter 3.11). Typically, one needs at least 10 tests to determine an indicative strength value and more than about 30 to determine the characteristic strength of a given product. Several methods may be used, which can

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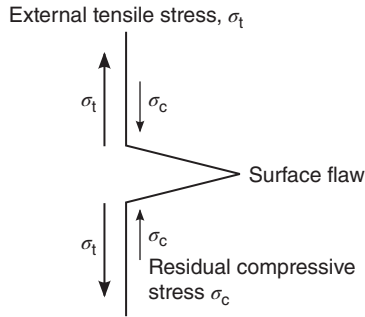


Figure 1 General mechanism of residual surface compression increasing the fracture strength.

be divided into bending- and impact-strength tests. The former involve two-, three-, or four-point bending or ring-on-ring test whereas the latter measure the ability of the material to absorb the impact energy of a falling object that is typically released by a dropping ball or a pendulum hammer.

The different tests are best suited for different products, e.g. two-point bending for glass fiber or thin glass sheet and four-point bending for architectural glass (EN1288-3). If one wishes to eliminate edge effects on the strength, then the ring-on-ring test is performed according to EN1288-2 or EN1288-5. Besides, different methods

Table 1 Comparison of thermal and chemical strengthening ("ion stuffing" process) [1]. Note that for chemical strengthening the characteristics depend on the ion-exchange treatment parameters as well as the treated glass.

Property	Thermal strengthening	Heat strengthening	Chemical strengthening
Maximum strength	120–400 MPa	70–150 MPa	150–1000 MPa
Residual surface compression	90–150 MPa	35–55 MPa	100–900 MPa
Core tension stress	50–80 MPa	20–30 MPa	20–60 MPa
Thickness of surface compression layer	Approximately 20% of the glass thickness	Approximately 20% of the glass thickness	Thin surface compression (normally <100 μm) unless treatment time lengthened
Treatment temperature	C. 75 °C above T_g	C. 75 °C above T_g	C. 100 °C below T_g
Mechanical treatment after strengthening	No cutting or drilling is possible	Cannot be safely cut	Might be cut or drilled or ground depending on the internal tension
Cost	Less expensive	Less expensive	More expensive (about 2–6 times)
Glass thermal expansion	The higher the better strengthening (e.g. $\alpha = 9 \times 10^{-6} \text{ K}^{-1} \gg 150 \text{ MPa}$ while $\alpha = 3 \times 10^{-6} \text{ K}^{-1} \gg 50 \text{ MPa}$ residual surface compression)	In the range of 6–9 to have a beneficial strengthening effect	Not important
Optical distortion	Heating and cooling must be carefully controlled to avoid distortion	Heating and cooling must be carefully controlled to avoid distortion	No significant distortion of ware
Spontaneously fracture	Yes	No	No
Time for treatment	Short time required (minutes)	Short time required (minutes)	Long time required (hours)
Sample thickness	Minimum 2 mm	Minimum 2 mm	0.2–15 mm
Shape	Not applicable to shapes where all surfaces are not freely accessible to chilling medium	Not applicable to shapes where all surfaces are not freely accessible to chilling medium	Applicable to unusual shapes as long as the glass surface can be in contact with the molten salt
Glass compositions	Applicable to most glasses	Applicable to most glasses	Alkali-containing glass compositions
Strengthening of abraded samples	No	No	Yes

Table 2 Characteristic tensile strength (95% confidence and 5% fractile) for glass in buildings. Average values of tensile strength can be up to ~70% higher.

Type of flat glass	Characteristic strength	Standard
Annealed window glass	45 MPa	EN 572-2
Heat-strengthened float glass	70 MPa	EN 1863-2
Fully tempered glass	120 MPa	EN 12150-2
Chemically strengthened float glass	150 MPa	pr-EN 13474-3

may give different characteristic strength values. For instance, one generally determines a higher characteristic strength in three- than in four-point bending experiments unless a proper correction is made for the position of the fracture origin. Besides, abrading samples prior to subjecting them to a bending strength test is advised if one wishes to compare the effects of different strengthening treatments.

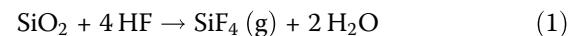
Internal stresses play a critical role in the intrinsic strength of a glass. Their measurements are thus of basic importance. They rely on the fact that optically transparent materials such as most oxide glasses exhibit the phenomenon of stress birefringence [3]: if planar or circular polarized light passes through a glass with residual stresses, the light wave is split into two other waves whose planes of polarization are parallel to the local principal stress directions. The two light waves travel through the glass at different speeds, which gives rise to a phase difference related to the in-plane stresses, governed by the stress optical coefficient of the material, i.e. by its stress dependence of the linear refractive index. Residual stresses in oxide glasses can therefore be determined from birefringence fringes measured by photoelastic methods such as differential surface refractometry (DSR), grazing angle spherical polarimetry (GASP), scattered-light polariscopy (SCALP), or polarization microscopy with a compensator such as of the Babinet, Babinet-Soleil, or Berek type. The stress profiles of strengthened glasses are important information as they control not only the ultimate strength of the material but also the pattern of fracture. Information such as the magnitude of compressive and central tensile stresses as well as the depth of the compressive layer can be studied in photoelastic measurements. These methods will likely be further improved as digital imaging, image processing, and new light sources become more readily available. It is also worth mentioning that finite element modeling (FEM) can be used to predict stress profiles although significant limitations still affect the boundary conditions of the available FEM models.

3 Elimination of Surface Flaws

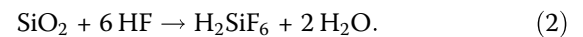
3.1 Polishing

There are many different methods to compensate, avoid, or neutralize surface defects. All have in common that they aim at smoothing the surface and reducing the effective defect size, but they all suffer from the fact that the strength improvement is only temporary if the glass is left unprotected after treatment. Traditional methods operate on the material at room temperature. CMP has long been a common route whereby the glass surface is polished by different slurries or plates containing abrasive (granular) material of different grain sizes. As indicated by its name, the method actually involves both chemical and mechanical mechanisms because the abrasives are applied to the glass in combination with liquids, such as water or oils, not only to avoid overheating but also to induce chemical reactions. The chemical reactions can be described in terms of erosion/corrosion mechanisms, e.g. diffusion reactions, glass dissolution under load, adsorption rate of dissolution products on the polishing grain, the rate of silica redeposition onto the glass surface, and the aqueous corrosion rate between particle impacts [4]. Depending on the target application, polishing is usually performed step by step from rough to fine with smaller and smaller abrasive grains. From coarse to fine, typical polishing abrasives are SiO₂ (sand), SiC (silicon carbide and carborundum), Al₂O₃ (corundum), CeO₂ (cerox), and diamond paste, cerox being in fact the major abrasive used because of its relative softness which provides high surface quality and relatively high material removal rate combined with a low degree of inherent scratching. For safety (and also aesthetic) reasons, it is common to grind/polish mechanically the edges of flat glass to render them plane, chamfered, or round. This operation is widely performed not only in the flat-glass industry but also for art and optical glasses.

Etching is a purely chemical process whereby polishing results from dissolution of the glass by aqueous solutions of hydrofluoric acid (HF), one of the few acids that efficiently dissolves silicates at room temperature. For pure SiO₂, the reactions are



and



As indicated by these reactions, attack by HF is not strictly an etching process, but rather a chemical dissociation reaction.

Owing to its broad versatility and very high reproducibility, HF etching has traditionally been used in the art-glass industry for producing extra clear and also matt or frosted surfaces. But the process is not always efficient to

remove surface defects and improve the strength of glass because of its relative slowness. In addition, HF is very toxic so that extreme precautions need to be taken when it is handled. In view of its toxicity and resulting problems in the work environment, it is now less used.

In the art-glass industry, etching has been complemented or partly replaced by fluid-jet polishing performed with versatile robots. Hereby, fluid-jet polishing is a generic term for many different techniques that all rely on the high-velocity jet formed when a pressurized fluid passes through a small nozzle. If the jet is projected onto a glass, some matter is removed by erosion to yield a smoother surface or, more often, to cut it more smoothly than by traditional mechanical means. Water or gases are generally used but abrasives can be added to the fluid to tailor the rate of material removal. Depending on the nature of the fluid, one distinguishes abrasive-jet (e.g. sand-blasting), abrasive-water-jet, and abrasive-slurry-jet polishing. Water-jet technology or hot-air jet technology can also be used to cut glass [5]. With water jets, both abrasive and nonabrasive cutting is possible. Hot-air jet cutting is based upon thermal-stress cleavage, where a scratch or a shallow cut is needed so that the hot-air jet causes thermal stresses to fracture the glass alongside this pre-scratch.

Other polishing techniques rely on self-healing of a glass rapidly heated up such that the nominally defect-free surface associated with fire polish is obtained. At temperatures higher than the transformation range, flaws are spontaneously eliminated through reduction of the surface area that results from minimization of the surface energy of the molten glass. Fire/flame polishing is frequently used in the production of household glass such as stemware and tumblers (Figure 2). The flame is most often oxidizing with a temperature of about 2000 °C such that the surface is quickly heated to softening temperatures in the 600–800 °C range. For stemware, fire/flame polishing is usually performed in three very fragile zones, namely, the junctions with the foot and the bowl, and the rim, which is especially vulnerable as it is cracked-off by thermal shocks produced either traditionally or with laser heating to ensure finer cuts.

For glass optical components that need a very fine polish, new, more sophisticated methods have been designed. Ion beam polishing, for instance, consists in a bombardment procedure with reactive ions (e.g. Ar⁺) at wide angles, leading to surface sputtering and, hence, flattening-out of surface roughness. Plasma polishing involves chemical reactions between reactive plasma and surface atoms of the glass. Magneto-rheological polishing process is based on magnetic manipulation of magneto-rheological slurries, which is controlled via computer algorithms. Finally, elastic emission machining



Figure 2 Flame polishing of the rim of stemware in a glass production facility (Sandvik Glassworks, Sweden).

is very similar to abrasive polishing with the main difference that it is controlled numerically.

3.2 Laser Heating and Cutting

In advanced glass production, high-power infrared CO₂, Nd-YAG, or diode lasers are now used to polish or cut glass. For polishing, the process is relatively similar to fire/flame polishing because it reduces the viscosity of the glass surface where defects are removed. Although it is a fairly recent technique, laser cutting has become relatively widespread for both flat and household glass. It is even making mechanical means obsolete for thin glasses because of the dramatic reduction of defects along the created edges (Figure 3). Another advantage is that it is a clean process compared to mechanical scribing, as it typically does not create debris.

As summarized in Table 3, laser cutting can be performed in different ways. One is very similar to the mechanical method in that a laser is used to scribe the glass surface before the second step of breaking [5].

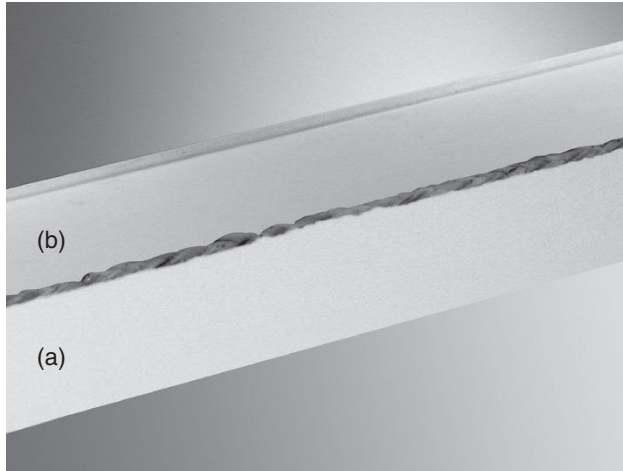


Figure 3 Contrast between the cracked edge of a 4-mm thick mechanically scribed float glass (a) and the smooth edge of a 2-mm thick laser-cut sample of another float glass (b). Special thanks to MDI Advanced Processing GmbH for providing us with the latter sample.

Cutting speeds of 1–2 m/s have been achieved with an Ar laser. Thermal-stress cutting is another method, suitable glasses thinner than 1 mm, whereby a crack is first initiated with a diamond tip or an ablation laser. The IR laser then locally heats the material in a predetermined path and builds in this way high compressive stresses inside it, which prevent the crack to propagate. A coolant water-jet beam then follows the path of the IR laser and turns the compressive stresses into high tensile stresses that cleave the glass.

With a third process, the glass is cut solely by laser ablation with the green or UV beam of (excimer) lasers, which can also chamfer the glass edge at the same time. A fourth method called filament cutting makes use of the shorter pulses of a green laser, thereby creating less heat than longer pulses and reducing the width of the heat-affected zone (HAZ). Filament cutting provides high edge-surface

quality at cutting speeds of about 0.5 m/s, which is still slow compared to mechanical scribing typically made at a rate of about 3 m/s. In summary, laser glass cutting is still a rapidly evolving technology that performs well for thin glasses, whose main disadvantage currently is the high investment cost of the instrument for a relatively slow cutting speed.

4 Thermal Strengthening

4.1 Compressive Stresses

Thermally strengthened glass is widely used in architectural applications (Chapter 9.1), in the transportation sector (Chapter 9.2), and is also very common for covers of photovoltaic and concentrated solar power modules (Chapter 9.4) with the important practical constraint that, because of its high strain-energy content, the material can no longer be subjected to any mechanical treatment. Thermal strengthening of containers and drinking ware is less common but is developing (Chapter 1.5) as the process is quick and not very expensive so that its cost may be offset by the various advantages resulting from weight reduction.

Thermal strengthening relies on the fact that glass, like most brittle materials, is strong in compression and weak in tension. In this process [6], the glass is rapidly quenched with dry or humid air, which is quite generally pressurized. Because the glass surface cools down and contracts more rapidly than the interior, the interior finds itself in compression whereas the surface is in tension. At T_g , the glass surface becomes an elastic solid while the hotter interior still is a viscoelastic body that can undergo structural and stress relaxation [7]. As the glass continues to cool down, the interior contracts and the glass surface are then placed in a state of compression by the contracting interior whose tensile stress eventually balances the

Table 3 A comparison of different laser cutting methods [5].

	Laser scribe and break	Thermal-stress cutting	Laser ablation	Filament cutting
Edge quality	Causes edge damage	Good	Poor surface finish	Relatively good
Scribing	Initiation required	Initiation required	Not required	Initiation required
Drawbacks	Balance of scribe and break speed	Precise thermal and stress fields needed	Deposits of melted glass	Difficulty to control the depth of microcracks
Drawbacks	Laser focused on a narrow line	Difficult to control at high speeds	Grinding/polishing necessary	Polishing may be necessary
Process steps	Two	Single	Two	Multiple scanning
Thickness range	Thin/thick glasses	Thin glasses	Thin/thick glasses	Thin glasses

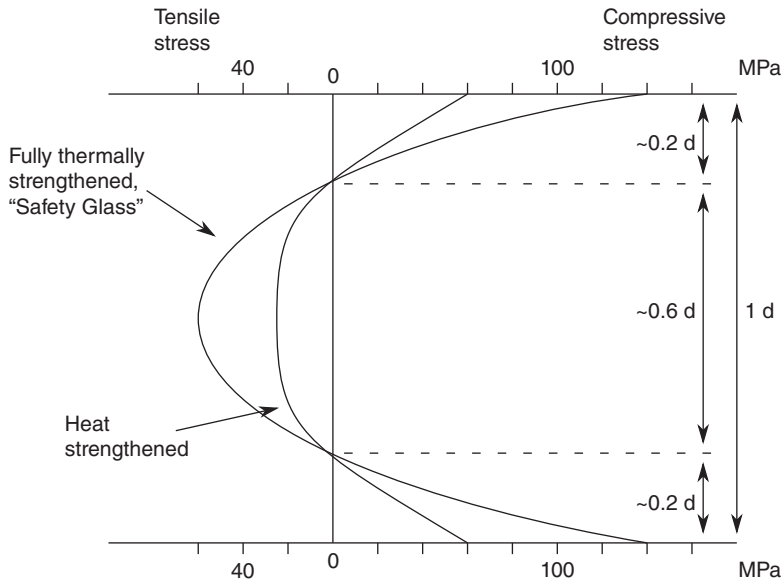


Figure 4 Schematic stress profiles of fully thermally strengthened (safety glass) and heat-strengthened glass; d is the thickness of the glass. Heat-strengthened glass is achieved by application of a slower cooling rate than for fully thermally strengthened glass.

compressive stresses at the surface. With the assumption of a truly parabolic residual stress profile, which is borne out by experimental data (Figure 4), one finds that the central tensile stresses are approximately half the value of the compressive stresses at the surface.

4.2 Tempering Processes

In practice (Figure 5), the glass is cooled within a few tens of seconds from a temperature higher than $600\text{ }^{\circ}\text{C}$ to ambient. During the first seconds, the temperature drops at the surface by more than $150\text{ }^{\circ}\text{C}$. Starting from a temperature T_0 about $75\text{ }^{\circ}\text{C}$ higher than T_g is of major importance in an industrial process: if T_0 were too low, it would cause the glass to fracture upon cooling whereas, if it were too high, the glass would not be stiff enough so that it would be marked by the rollers when beginning to cool down. Importantly, the rapid cooling required must be relatively uniform to prevent too large tensile stresses from developing at the surface. For this reason, all surfaces must be freely accessible to the air jets when strengthening glasses with complex geometries. Thermal strengthening thus depends on the thermal expansion of

the glass, the quality of the parent glass, the maximum cooling rate practically achievable, and the availability of freely accessible surfaces. Soda-lime-silicate glass is most commonly used; float glass being, for instance, standardized by EN 572-2 for architectural applications.

Theoretically, the highest cooling rates allow highest compressive stresses to develop in the glass surface and thinner glass to be strengthened. Upon too fast cooling, however, the initial thermal gradient and surface tensile stresses can become so large as to cause glass fracture. The temporary tensile stresses which develop at the glass surface during cooling from the initial temperature (T_i) to T_g ($\Delta T = T_i - T_g$) can be estimated from Eq. (3) [8],

$$\sigma_i = \frac{E\alpha}{1-\nu} \Delta T = \frac{E\alpha}{1-\nu} \left(\frac{d^2 R}{8k} \right), \quad (3)$$

where E is the elastic modulus, ν is Poisson's ratio, α is the thermal expansion coefficient, d is the thickness of the glass, k is the thermal diffusivity, and R is the cooling rate (noteworthy, all in the range immediately above T_g). As seen from Eq. (3), the amount of temporary tensile stress depends to a large extent on the thickness and on the cooling rate; however, thermal relaxation also matters.

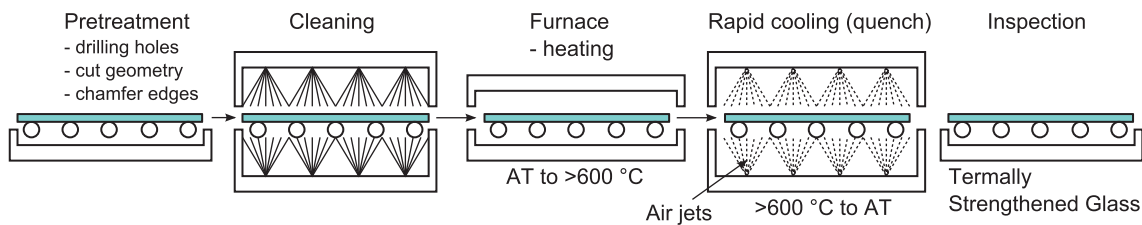


Figure 5 Process scheme of the thermal strengthening process (AT = ambient temperature).

For stress relaxation, the following estimation may be used:

$$\sigma_r = \sigma_i \exp(-\tau E / 6(1-\nu)\eta), \quad (4)$$

where σ_r is the relaxed tensile stresses, τ is the observation time, and η is the viscosity. With conventional cooling rates, the temporary tensile stresses are about 40 MPa. For thinner glass, greater cooling rates are needed. In Figure 6, the developed stresses of a thermally strengthened soda-lime-silicate glass are modeled for a given cooling rate, illustrated as a function of glass thickness. As the glass becomes thinner, the cooling rate is not sufficient to develop the same magnitude of stresses. To demonstrate the importance of the cooling rate, the residual stress profiles are also plotted (Figure 7) as a function

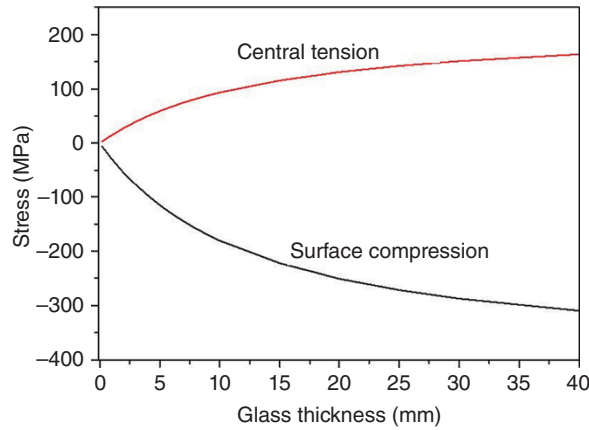


Figure 6 Calculated residual surface and central stresses as a function of the glass thickness for a given cooling rate of a typical soda-lime-silicate glass.

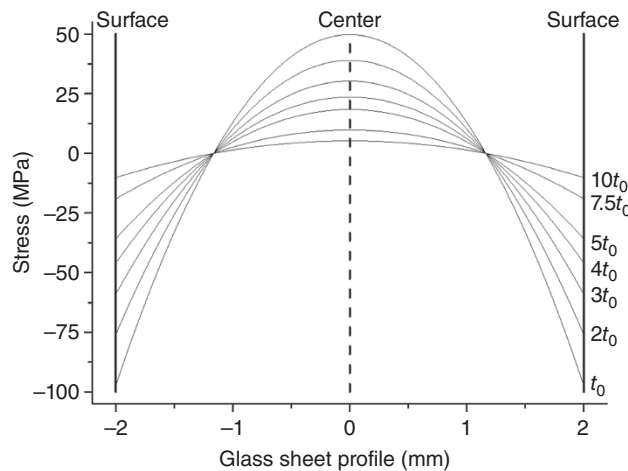


Figure 7 Residual stress profile for a given thickness as a function of cooling rate, t_0 is the critical time, i.e. the time that it takes for the center of the glass to be the same temperature as the surface. For a 4 mm glass, t_0 is 4.041 seconds for a typical soda-lime-silicate glass.

of cooling rate for a 4 mm soda-lime-silicate flat glass. As the cooling rate decreases, or the critical time to cool from T_i to T_g increases, the developed compressive stresses in the surface becomes lower.

4.3 Strengthening Limitations

In general, therefore, there is a critical limit to the thickness of the glass that can be thermally strengthened by conventional processes. Commonly, 3 mm was considered minimum but a strengthening process for 2 mm or thinner glass has recently been developed. In this state-of-the-art process, the rollers are replaced by gas flotation systems in the furnace (e.g. the HZL technology of the LiSEC group and Glaston's GlastonAir™). In this respect, eliminating the ceramic rollers is very important because they readily introduce surface defects onto the glass such as roller waves or scratches, thereby increasing the susceptibility to fracture, and also may act as heat sinks during quenching.

Fully thermally strengthened glass is also called *safety glass* because it fractures into small fragments, which are in general much less sharp and dangerous than the large dagger-like pieces of broken annealed glass. This important feature results from the balancing tensile stresses in the interior, i.e. the large amount of strain energy. When thermally strengthened glass fractures, the strain energy is rapidly released through the creation of the new surface of small blunt fragments. A smaller fraction is released as sound, heat, and kinetic energy in the fragments. The strength of thermally strengthened glass increases linearly with central tension whereas, as

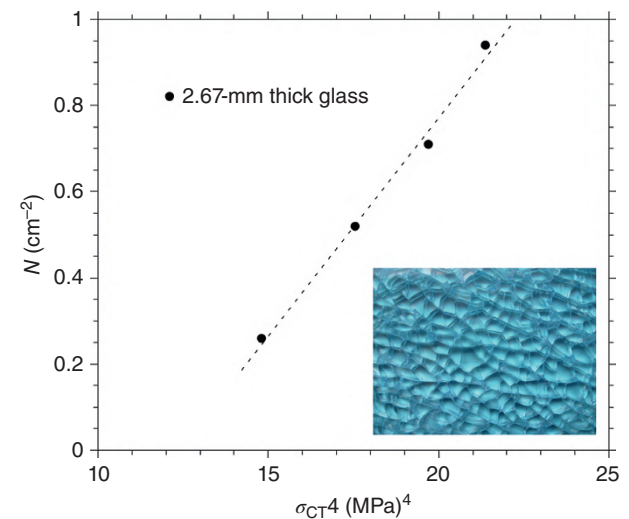


Figure 8 A plot of the number of fragments per square centimeter as a function of the fourth power of central tension, data taken from [9]. The inset shows a fractured thermally strengthened glass, it is not linked to the data.

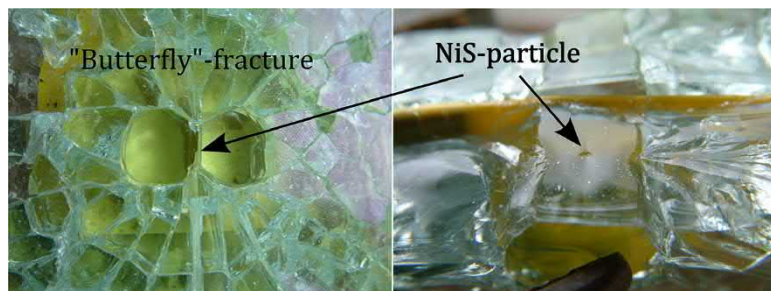


Figure 9 Typical “butterfly” fracture pattern (to the left) with the origin of a NiS particle (shown to the right). Special thanks to John Colvin, Glass Consultant, for providing the photos.

illustrated in Figure 8, the frangibility (strain energy) increases as the fourth power of central tension [10]. In contrast, a lower degree of strengthening is achieved for the standardized *heat-strengthened* glass, which is also thermally strengthened but with a slower cooling rate and lower central tensile stresses so that its fracture pattern resembles that of annealed glass.

Several standards have been developed for commercially used thermally strengthened glass in buildings, e.g. EN 12150 for fully thermally strengthened glass, EN 1863 for heat-strengthened glass, and ASTM C1048-12e1. They describe dimensions, fracture characteristics, flatness tolerances, and physical characteristics (such as thermal durability, mechanical strength, and iridescence) of thermally strengthened glass. The degree of thermal strengthening is also standardized. In Europe, according to EN 12150-1, the glass is fractured in a controlled manner and the number of glass fragments in a standard area is counted. The residual stress profile can be deduced from the number of glass fragments, typically it ranges from 0.6 to 1.6 numbers of fragments per square centimeter for fully thermally strengthened glass depending on the thickness of the glass. The degree of strengthening ensured by heat-strengthened glass (standardized in EN 1863) is characterized instead by an area/mass criterion for both small fragments and medium-sized fragments. There is also an ASTM standard, C1279, where the surface and edge stresses are standardized. It involves a nondestructive photoelastic measurement of the surface compressive stresses with the DSR, GASP, or SCALP techniques mentioned in Section 1, the surface compressive stresses are s .

4.4 The Problem of Nickel Sulfide

Fully thermally strengthened glass suffers from another major problem when nickel is introduced into the glass as a contaminant of the raw materials, most likely in the form of stainless steel fragments. In the glass melting process, nickel then reacts with sulfur impurities to form NiS inclusions whose size ranges from 0.05 to 0.6 mm. Under equilibrium conditions, nickel sulfide should transform below about 390 °C from a high-temperature

(α -NiS) to a low-temperature (β -NiS) phase. When the glass is rapidly cooled, however, the kinetics of the transition is too slow for α -NiS to transform into β -NiS. The α -phase thus remains metastable until, after a time that depends on thermal history and possible exposure to solar radiation, the transition eventually takes place irreversibly at ambient temperature. If the NiS is located in the central tension zone, the volume increase of 2–4% caused by this transition may then cause spontaneous fracture of the glass even when the inclusions are too tiny to be visible. A “butterfly” fracture pattern (Figure 9) may be observed in such cases. Owing to the importance of these inclusions, a standardized, heat-soak test (EN 14179, DIN 18516) has been designed to detect their presence. It consists in heating the glass for a minimum of two hours at 290 ± 10 °C, a temperature at which the NiS phase transformation is greatly accelerated.

5 Chemical Strengthening

5.1 An Expanding Method

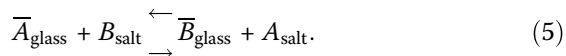
Chemical strengthening is the other main process with which compressive stresses are generated in the glass surface. It is the term commonly used to describe the effects of *ion stuffing*, namely of $K^+ - Na^+$ and $K^+ - Li^+$ or $Na^+ - Li^+$ ion exchange in sodium- and lithium-bearing glasses, respectively. There is not a unique and generally accepted definition of chemical strengthening, however, because the same term also designates processes through which stronger glasses result from differences in thermal expansion coefficient between the surface and subsurface [1].

Chemically strengthened glass windshields for automobiles were already marketed in the 1960s by General Motors, but these were not a success, mainly for cost reasons, at the time the newly evolving float glass was being widely adopted (Chapter 1.4). From 1971, however, most spectacle lenses in the United States have been strengthened in this way to withstand the minimum impact-load conditions prescribed by the Federal Drug Administration. Whereas chemically strengthened glass found numerous applications in the air, naval, military,

automotive, locomotive, electronic, and architectural sectors [1], its more recent, extensive uses in electronic displays has made its presence more widely felt in the general public (Chapter 6.10). In recent years, this increasing demand has led large producers of specialty glasses to launch commercial products from float glass (Chapter 1.4), e.g. Schott Xensation™ series, AGC, Dragontrail™, or by the fusion downdraw process, e.g. Corning® Gorilla® Glass and NEG Dinorex™ series.

5.2 Ion-Exchange Diffusion

Ions are exchanged when a glass containing a rather mobile ion, A, is exposed to a concentrated source of another mobile ion B so that A ions diffuse out of the glass to be replaced by B ions from the source as described by the reaction



For cost and melt stability reasons, the source is typically a molten salt with which the glass interface instantaneously achieves a close contact (Figure 10). The reaction takes place under thermodynamic conditions such that the activation energy for the exchange reaction may be overcome and the kinetics of the reaction are fast enough to be acceptable from a practical standpoint.

In general, several ions can be exchanged through reactions that are kinetically described by Fick's laws for diffusion of equally charged ions. Referring to Frischat [12] for extensive information on these reactions, we will focus here on alkali exchange and dealkalization (i.e. replacement of alkali ions in the glass by hydronium ions).

The inward and outward diffusing ions have different sizes and should, therefore, have different mobilities in the glass. The more mobile ones will tend to outrun the less mobile, causing an internal electric field in the glass. This field slows down the former ion and accelerates the latter until both have equal mobilities. In general, this interdiffusion process can be described by an effective interdiffusion coefficient $\bar{D}$.

$$\bar{D} = \frac{D_A D_B}{\gamma_A D_A + \gamma_B D_B}, \quad (6)$$

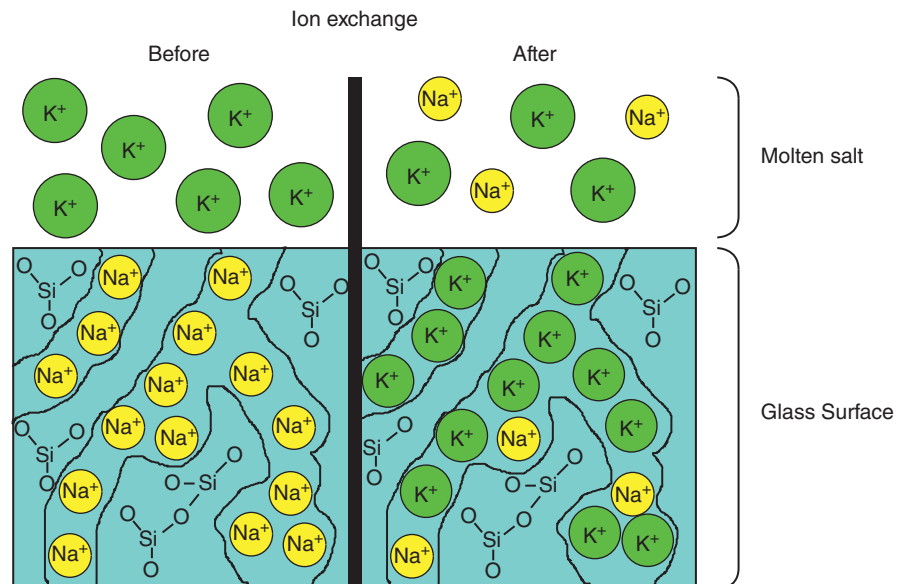
where D_A and D_B are the diffusion coefficients of the two ions and γ_A and γ_B are the local ion mole fractions (Chapter 4.4). The ion-exchange interdiffusion coefficients can be determined in several ways if the proper boundary conditions for the solution of Fick's second law are applied.

Alternatively, one can enhance diffusion within the glass by other methods than thermal activation through the effects of an external electric field, of X-ray irradiation, or of microwaves. In general, enhancing interdiffusion also enhances thermal relaxation so that the result may not be useful when it comes to induce surface compressive stress. In addition, electric-field-assisted ion exchange is restricted to one side only of the glass piece, which may be disadvantageous for some applications.

5.3 The Ion "Stuffing" Method

Ion stuffing usually designates the most common chemical strengthening process. This batch process involves thermally assisted ion substitution of a smaller ion in the glass by a larger ion from a molten salt. By being

Figure 10 Schematic ion-exchange process (Source: Redrawn from [11])



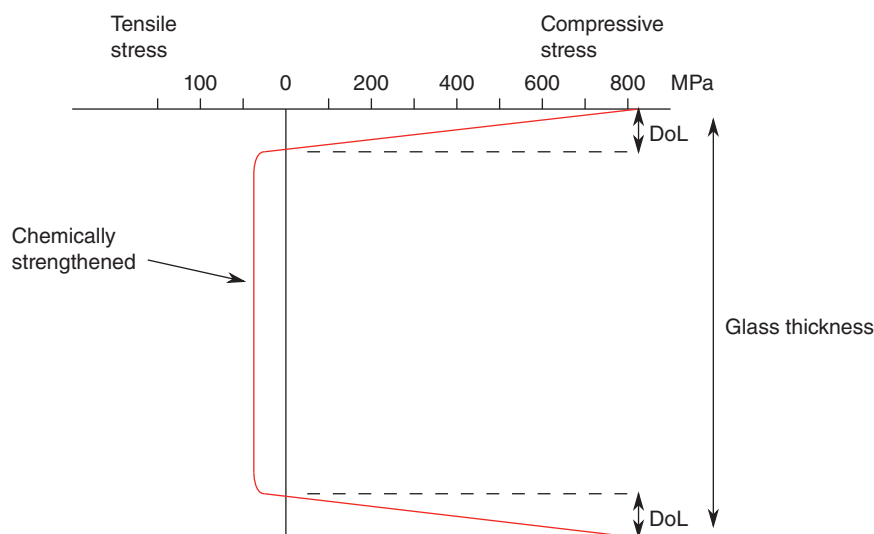


Figure 11 Principal stress profile for a chemically strengthened aluminosilicate flat glass. The scale bar values are only indicative.

literally squeezed into the surface (Figure 10), the larger ion induces residual compressive stresses in the glass surface that seal defects as illustrated by the stress profile shown in Figure 11.

As ion stuffing is a diffusion-based process, it depends on temperature and time, being generally much slower and, therefore, about 2–6 times more expensive than thermal strengthening. The degree of compressive stresses induced by the incorporation of larger ions is mainly determined by the linear network dilatation coefficient whereas the depth of the compressive layer (DoL in Figure 11) is limited by the kinetics of interdiffusion [13]. Ions are usually exchanged for 2–24 hours at temperatures of at least 100 °C below the glass T_g in order to minimize stress relaxation during the process and to avoid any deformation caused by softening of the glass. As a result of ion exchange, the thermal expansion coefficient of the glass surface may be altered but the resulting effect is relatively small compared to that of “stuffing.”

Commonly, ion-stuffing strengthening involves Li^+ - or Na^+ -bearing glasses exchanged with Na^+ and K^+ , respectively. Notwithstanding their very high cost, Rb^+ or Cs^+ is not used because their still larger size would cause them to interdiffuse too slowly. The interdiffusion rate depends to a great extent on glass composition. The highest rates are generally found for alumina- or zirconia-containing glasses [11]. High enough alkali contents are also an important factor as chemical strengthening requires significant ion exchange whereas mixed-alkali glass compositions have a beneficial effect on the rate of interdiffusion [14]. Typically, glass compositions having a $\text{R}_2\text{O}/\text{Al}_2\text{O}_3 \approx 1$ molar ratio have a high rate of interdiffusion related to a low fraction of non-bridging oxygens (NBOs) [15]. Likewise, Varshneya [14] has suggested that higher compressive stresses can be achieved for glass compositions

having a greater network connectivity (along with in general a high Young modulus). The same applies to other minor constituents in the glass composition such as MgO .

The molten salt chemistry has also a strong influence on the kinetics of ion exchange. Whereas progressive contamination of the molten salt by the glass itself slows down the ion-exchange kinetics, there are indications that small salt constituents, such as alkaline earth ions [16] or hydroxide ions [17], have the same effect as a result of ion exchange with the glass for the former and of induced structural rearrangements or chemical reactions for the latter.

In summary, the efficiency of the ion-exchange process as well as the residual compressive stresses depend on several basic factors, the main ones being (i) the temperature dependence of the interdiffusion coefficient; (ii) the time of exchange; (iii) the nature of the glass-salt interface; (iv) the salt-bath chemistry; (v) the glass composition; (vi) the exchanging pair of ions; and (vii) the effect of temperature on viscous and structural relaxation.

Depending on these factors, the thickness of the compressive layer can be varied from tens to a few hundred microns. The tensile stresses in the interior typically range between 20 and 60 MPa and depend on the magnitude of the surface compression, the DoL, and the sample thickness. As to the fracture pattern, it depends on the same factors because it is a direct function of the magnitude of the tensile stresses in the interior. When fracture occurs, it usually yields fairly large sharp splinters but one can minimize the danger by sticking a thin plastic foil onto the glass surface. Although most chemically strengthened glasses can be cut either mechanically or with a laser, the created edges have much less strength since they are deprived of compressive stress.

Chemically strengthened flat glasses are standardized according to the norm ASTM C1422, which classifies the product by DoL and magnitude of surface compression. The ASTM C1422M-10 prescribes a standardized method to measure the stress profile of chemically strengthened glass with a polarization microscope and optical retardation compensation procedures. Chemically strengthened glasses are known to be very resistant to scratches in a way that depends on the DoL and on the magnitude of surface compressive stresses.

Finally, a more complex two-step ion-exchange process has been designed whereby the first is used to induce compressive stresses before the second either reintroduces the original ion or introduces a new one in the outermost surface layer. This two-step ion-exchange is used for making Engineered Stress Profile (ESP) glasses [18] whereby an ion such as K^+ is introduced in a sodium-bearing glass and at the end Na^+ ions are reintroduced. As a result, the surface is weak and cracks can grow and even become visible before they are arrested by the compressive zone somewhat beneath the glass surface, i.e. the glass does not depend on the size of the surface flaws. These ESP glasses were developed to be used for architectural purposes and designed to give a hint prior to catastrophic fracture occurs. It is noteworthy that similar processes have been developed for gradient index optics to produce a gradient in optical polarizability which leads to a gradient in refractive index.

Recently, work has been done on the strengthening effect of water treatment of glasses, which is another type of ion stuffing. Fett et al. [19] showed that considerable strengthening is obtained with the residual compressive stresses achieved as a result of an exchange of H_3O^+ for Na^+ ions. Likewise, Lezzi et al. [20] strengthened silica-glass and E-glass fibers by water vapor treatments of bent fibers, an effect explained in terms of H_3O^+ ion exchange and surface stress relaxation.

5.4 Differential Expansion Strengthening

Compressive stresses at a glass surface most simply result from the elastic resistance of the glass to volume changes induced by ion exchange, but they can also be created from temperatures above T_g from changes in the temperature derivative of volume, i.e. in the coefficient of thermal expansion (CTE). Upon cooling, the high-CTE layer tends to contract more than the low-CTE, putting the latter under compression. The simplest strengthening technique consists of cladding a low- over a high-CTE glass [11]. If the thermal-expansion differences are too large, however, very sharp stress gradients form at the interface so that the glasses are easily cracked off from each other. As with cladding, one can achieve the same effect by replacing sodium in the glass surface with

lithium in high-temperature ion-exchange strengthening. But the drawback of this process is that the glass surface generally becomes translucent within minutes because of surface crystallization whereas the strengthened glass may in addition deform under the high compressive stresses achieved. With TiO_2 as nucleating agent, the method is thus generally limited to special glass compositions such as aluminosilicate glasses in which beta-spodumene crystals precipitate as a result of Li^+ introduction in the glass via ion exchange.

Another type of strengthening technique relying on differences in CTE is dealkalization. It is based on the replacement of Na^+ by hydronium ions, H_3O^+ in the glass surface layer [12]. Dealkalization occurs when acidic gases such as HCl , SO_2 , or SO_3 react with sodium from the glass [21]. The surface layers are generally relatively thin although their thickness again depends on many factors such as temperature, treatment time, and glass composition. In general, dealkalization treatments affect the chemical durability to a larger extent than it strengthens the glass. It has previously been widely applied to container glass [22].

6 Strengthening by Coating

6.1 General Principles

One can also increase strength by coating the glass to protect chemically or physically its surface. Lacquers such as Teflon, Lexan[®], polyacrylates, and silanes represent an effective barrier and provide a chemically inert environment at the vicinity of the crack tip [23]. Mechanical protection is conferred by coatings such as SnO_2 and amorphous carbon that increase the scratch or abrasion resistance. In both cases, however, the strengthening mechanisms at work often remain insufficiently understood.

With coatings based on sol-gel and epoxy systems, one can alternatively reduce the effective lengths of cracks at the glass surface. Much of the work done on coatings that fill surface defects has been performed on deliberately abraded (e.g. sand-blasted) glass substrates containing relatively large controlled defects. As the recovered strengths remain well below the theoretical values, the conclusion is that only larger flaws are successfully penetrated by the coatings [24]. It is important, therefore, not only that the coatings have low enough viscosities on application to penetrate flaws but also that they develop a strong adhesion to the glass. For epoxy-based coatings, strengthening could be due to residual stresses arising from the thermal expansion mismatch of coating and closure of glass surface defects [25]. But most coatings used to fill surface defects tend to be too thin to prevent subsequent contact damage.

6.2 Sol-gel Coatings

The strength of glasses can be improved in different ways by sol-gel coatings, which fill surface defects, blunt crack tips, clamp crack sides, add a compressive stress to the surface, protect the material from fatigue, or form a barrier to moisture (Chapter 8.2). These coatings are typically used in the flat- or household-glass industries as well as in optical applications to yield reflective or antireflective surfaces, optical waveguides, and nonlinear optics. Most prominent are, for instance, tetraethoxysilane (TEOS)-derived silica coatings because they enhance the strength of silica glass by 120–130% whereas the strength of soda-lime-silica glass can improve by factors of up to three with polysilazane-derived coatings [1].

Sol-gel processes include two different methods, one based on gelation between colloidal particles in a sol and another on hydrolysis and polycondensation of alkoxide, nitrate, or oxychloride precursors (Chapter 8.2). In both processes, the solutions are dried and then sintered to form dense amorphous solids. In principle, any type of multicomponent oxide can be synthesized from the relevant alkoxides by the sol-gel process. For application onto glass substrates, the most common methods are dip, spin, spray, flow, roll, and capillary coating but electrophoresis and ink-jet printing are also used. The sol-gel coating process has several advantages such as simplicity, low processing temperature, low-cost capability for large surface areas, ease of application onto a variety of substrates, and suitability for forming uniform and homogeneous films with a sub-micrometer thickness or a high optical quality [1]. On the other hand, thicker coatings ($>1\ \mu\text{m}$) have the disadvantage of tending to crack, leaving areas open for contact damage. Examples of hybrid coatings also exist where inorganic sol-gel coatings are combined with a cross-linked polymer resin.

6.3 Other Coatings

Hot-end and cold-end coatings are commonly applied to glass containers to reduce surface damage of the glass (Chapter 1.5). Hot-end coatings typically consist of deposited SnO_2 or TiO_2 , which increase the abrasion resistance. Cold-end coatings are lubricants such as stearates, oleates, and polyurethanes; the increased lubricity reduces the extent of surface damage during packaging and transportation [23].

Acrylate coatings are traditionally applied to silica optical fibers immediately after drawing because they represent a good chemically protective barrier and they are also thick enough to prevent subsequent contact damage (Chapter 6.4). Acrylate coatings have also been investigated for strengthening of flat glass for which they have been demonstrated to be somewhat effective.

There are a vast number of different functional coatings based on methods such as chemical vapor deposition (CVD), particle vapor deposition (PVD), Sputter deposition, and pulsed laser deposition many of which influence the strength of the glass (Chapter 6.8). Guardian's coating DiamondGuard[®] is, for instance, a patented deposited carbon coating whose properties resembles those of diamond. It has been stated to increase the scratch resistance of the glass through the coating's low coefficient of friction.

Epoxy coatings can potentially be used in the flat-glass industry for edge-strengthening or large-area protective coatings, e.g. photovoltaic modules, automobile wind-screens. Besides, CVD and PVD coatings are widely used in the flat-glass industry, mainly, however, for functional purposes rather than for increasing the strength.

7 Perspectives

In recent years, strengthening of oxide glasses has tremendously improved even though the theoretical limits, which are higher than 20 GPa, are far from being approached. Much progress, in particular, remains to be made for thin glass, which raises many difficulties. In a general way, the first improvement to be achieved concerns the quality of flat glass as defects not only degrade strength but also strongly limit the ability to strengthen thermally glasses thinner than 1.5 mm because of cracking. Second, for thermal strengthening, the cooling rate needs to be increased to increase the fictive temperature of the material which might increase the risk of producing visible faults. As some glasses do not have the appropriate thermal expansion coefficients to be thermally strengthened, it could be possible to optimize the glass composition to remedy this problem and, thus, to increase the damage resistance of the glass. Another important issue is quality control. It would, for instance, be valuable to control reliably at a reduced cost the strengthening level by other means than fracturing the glass and counting pieces. Likewise, detection of NiS inclusions is of major importance so that an alternative to the heat-soak test could reduce costs considerably.

For chemical strengthening, the glass composition should be further optimized with respect to diffusion, stress buildup, and contact resistance of the glass itself, where the time needed for ion exchange remains the major limitation. Also a better structural understanding of the glassy network during the chemical strengthening process should help to understand better how to increase diffusion rates and the subsequent buildup of compressive stresses as well as how to decrease thermal relaxation as a the trade-off between high ion-exchange temperature

and low rate of stress relaxation. The salt-bath chemistry is also very important. Whereas a better understanding of the poisoning effect of minor contaminants is needed, the composition of the salt bath should be adjusted to each glass composition. Furthermore, innovations are needed to design automatic and online processes, which would make the process less expensive.

Coatings will likely be a future key in protecting oxide glasses from abrasion and possibly also for strengthening purposes. There are a vast number of coatings and a more complete overview of their effects for protective and strengthening purposes is needed. Furthermore, the strengthening mechanisms and the role of coatings need to be better understood.

As first discussed by Rawson [26], control of the structural anisotropy of glass is yet another type of strengthening. The glass surface defects has a major impact on the glass strength, however, increasing the intrinsic glass strength may also significantly influence the practical strength of glasses (mainly glass objects with lower effective surface area such as fibers). Recently, there has been some evidence that the drawing stress of continuous basaltic and E-glass fibers affects the structural anisotropy and that the tensile strength of the fibers can be correlated to the structural anisotropy [27]. Another example is the forming of heterogeneous phases in glass by femtosecond pulse laser irradiation [28]. There is yet much to be studied regarding controlling the structural anisotropy.

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3.13

Radiation Effects in Glass

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1 Introduction

That glass color can be affected by sun light was noticed by Michael Faraday (1791–1867) in 1824. This was the first reported observation on the effect of radiation on a glass property, as emphasized by Edmond Becquerel (1820–1891), an authority on luminescence [1] and the father of Henri, the discoverer of radioactivity. Much more severe radiation-induced damage was then detected very early in radioactivity studies when the Irish geologist John Joly (1857–1933) observed in 1907 *pleochroic haloes* around minerals emitting α rays (Figure 1) [2]. Joly understood that the sizes of haloes were proportional to bombardment duration. With the help of the famous Ernest Rutherford (1871–1937), he thus used the extent of damage as a very simple method to date rocks. Of course, the very long geological periods are not relevant to the limited lifetime of man-made products. In view of potentially much more severe conditions of use, a significant question is the ability of glasses to withstand high levels of irradiation either by photons ranging from ultraviolet to gamma or by particles such as neutrons, electrons, protons, and heavy ions.

Important applications include not only nuclear-waste storage in chemically complex glass matrices (Chapter 9.12) but also numerous optical devices. In photonics, continuous-wave or nanosecond-UV lasers used for Bragg gratings inscription are, for instance, used to develop high-speed and multiplexed links in germano-silicate optical fibers for data transfer and sensing. Likewise, the utilization of femtosecond lasers for the

design of 3-D optical components in bulk materials has become an active and promising field. Whereas glasses withstanding high levels of radiation are required for a large number of applications operating in radiation-rich environments, radiation-sensitive glasses are, in contrast, of major interest for detection and dosimetry according to the principles laid down by Joly and Rutherford [3].

In oxide glasses, the network is composed of a polyhedral arrangement of glass formers connected by oxygen atoms (Chapters 2.4–2.6). Radiation can affect the local- and medium-range orders of the glass network either by an accumulation of point defects generated by electronic collisions or, directly, by nuclear collisions that cause displacement cascades and, therefore, some modifications of the atomic arrangement (Figure 2).

Because glasses are metastable phases, the question also arises as to whether the absorption of energetic radiations can trigger transitions toward states of lower enthalpy. No general answer can be given, however, because radiation-induced phase transitions, such as crystallization, have not been studied in a systematic manner except for silica. The main effects investigated have been those of electronic and nuclear collisions on silicate and borosilicate glasses. These are so diverse, however, that reviewing them all would be far beyond the scope of this chapter. In the field of femtosecond lasers, modifications depend on glass composition and on too many laser characteristics (wavelength, pulse duration, repetition rate, etc.) to be addressed here.

Interest will focus instead on the effects of ballistic interactions (atomic displacements) and ionizing radiation. Point defects will be first presented and attention will also be paid to the resulting changes in the structure of the glass network along with their consequences on density and bubble creations. In view of the importance

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Figure 1 Bombardment damage in a Norwegian Gneiss by α rays emitted by uranium-rich muscovite mica as seen by dark haloes termed *pleochroic* because, under polarizing light, their color varies with their orientation. Source: Photo Nicole Santarelli.

of optical applications, irradiation effects on light attenuation, refractive index, and redox state of rare earth (RE) ions will then be dealt with. Finally, the mechanical properties will be addressed in the context of nuclear waste storage, and approaches for hardening glasses will be presented.

Of course, the magnitude and kinetics of the changes observed depend on the nature and energy of the radiation (e.g. X and γ rays, neutrons, protons, and heavy ions).

For quantification purposes, the dose (or fluence) has been defined as the total energy brought to a unit mass of the material of interest (e.g. silica) and is expressed in Gray (Gy) units, i.e. $1 \text{ Gy}(\text{SiO}_2) = 1 \text{ J/kg}$ of silica glass. The dose rate (Gy/s) then is simply the ratio between the dose and exposure time, whereas a former unit, the rad ($= 0.01 \text{ Gy}$), remains widely used especially in the space-research community.

2 Point Defects

Over the last 50 years, numerous studies have been devoted to the nature, generation, and bleaching mechanisms of point defects in pure and doped silica glasses. After having first been mainly experimental, these studies now strongly benefit from multiscale simulation tools (e.g. [4]). Their results have been useful to design optical lenses, windows, mirrors, or other devices made up of silica, either pure or doped, with elements such as Ge, P, F, B, or N to tailor refractive-index profiles in single- or multimode waveguides.

Point defects in silica can be generated either by conversion of precursor sites into optically active defects or by the rupture of bonds such as Si–O–Si. Sometimes called color centers, these defects are associated with absorption bands generally peaking in the ultraviolet and the visible even though a limited number of defects do absorb in the

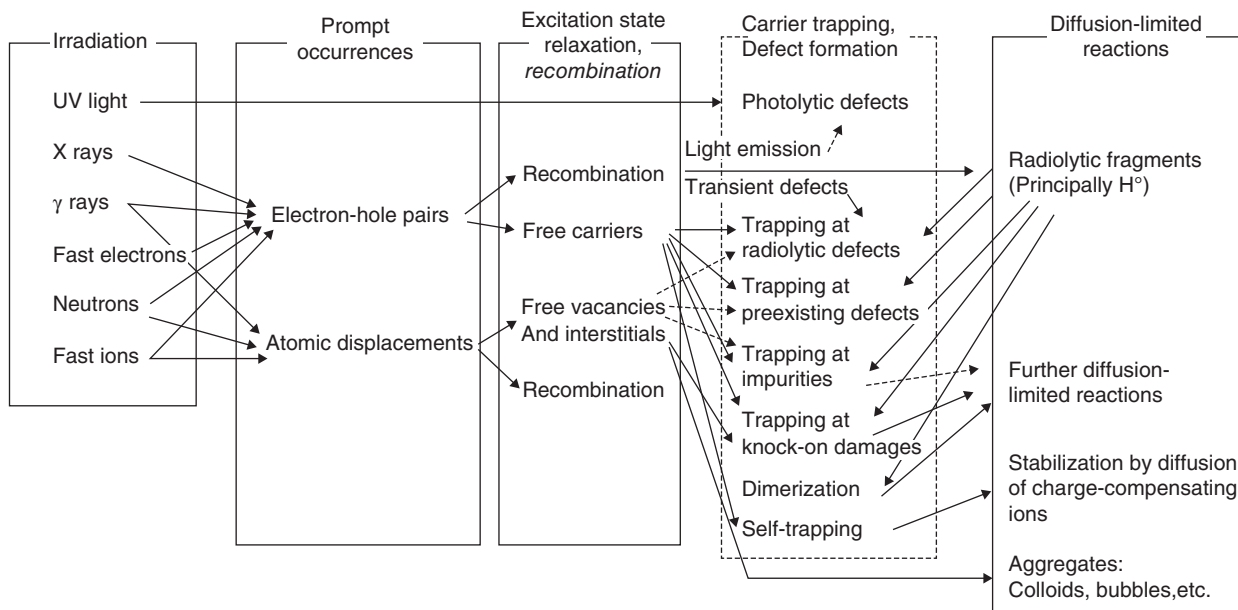


Figure 2 Irradiation defects in silica glass (from [4, 5]). (a) Main intrinsic point defects: ODC (oxygen deficiency center), E' (silicon dangling bond), NBOHC (non-bridging oxygen hole center), POR (PerOxy radical), and STH1 and 2 (self-trapped holes type 1 and type 2). (b) Isochronal annealing curves for some of these defects (c). Main optical absorption/photoluminescence excitation bands and emission bands of defect centers in the bulk (top) and at the surface (bottom).

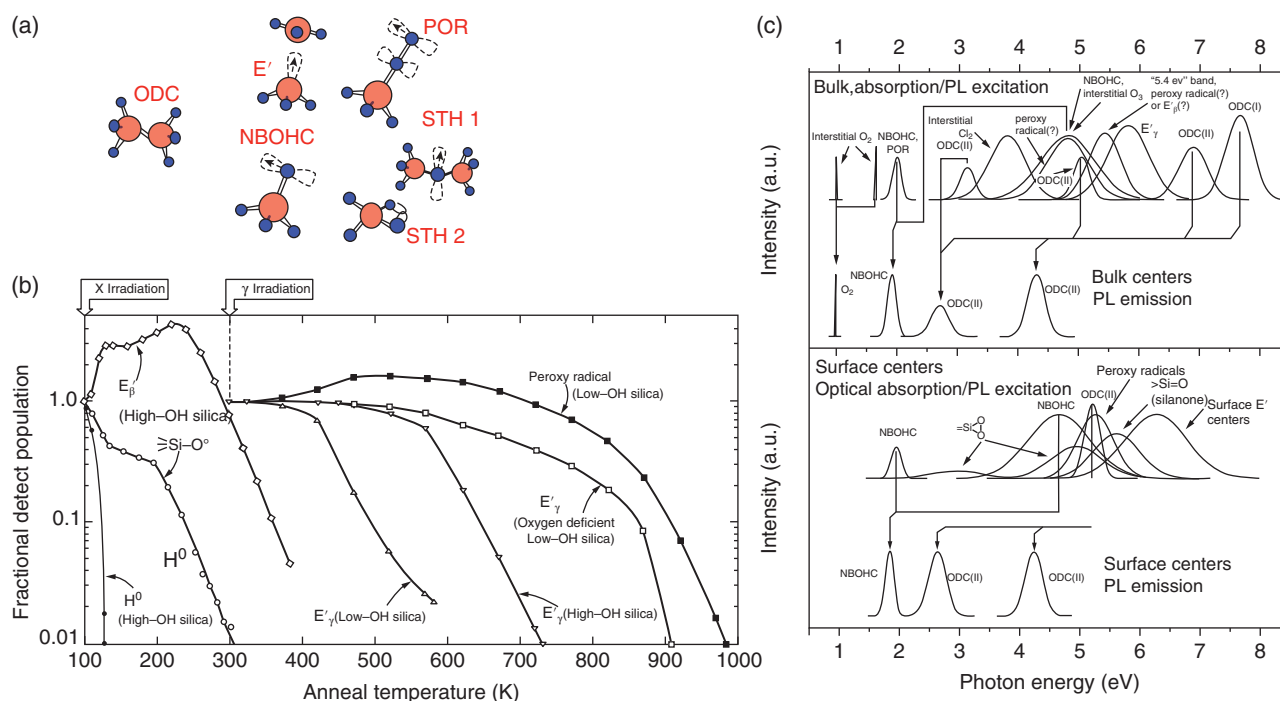


Figure 3 Radiation-induced mechanisms in silica-based materials upon exposure to different types of radiations (Source: Modified from [4]).

infrared. A fraction of these defects, either trapped electrons or holes, is also an emitting center. This feature accounts for the luminescence observed under irradiation, as depicted in Figure 3 for the defect structures and their associated optical absorption and photoluminescence bands [5]. Also shown in this figure is the slow decrease of the concentrations of some silica-related point defects upon thermal treatments in irradiated silica samples with either large or low amounts of hydroxyl groups. This evolution illustrates another important property of point defects, namely, their thermal stability that influences both their concentration and their kinetics of formation or annihilation under irradiation.

Numerous other parameters (Figure 4) determine the generation and bleaching efficiencies of the various point defects and, thus, control the radiation-induced attenuation (RIA) and its kinetics in terms of growth and dose dependence at the operating wavelength(s) of the application. Some of these parameters are intrinsic to the glass. This is of course the case of composition (including doping elements and impurities such as hydroxyl groups), stoichiometry, and, for example, the core and cladding sizes in fiber optics (Chapter 6.4). In silica-based glasses, phosphorus doping is particularly interesting because, even at concentrations as low as few thousands of ppm, it strongly increases the level of RIA in the visible and infrared via the creation of numerous kinds of point defects. Indeed, at least eight varieties of paramagnetic

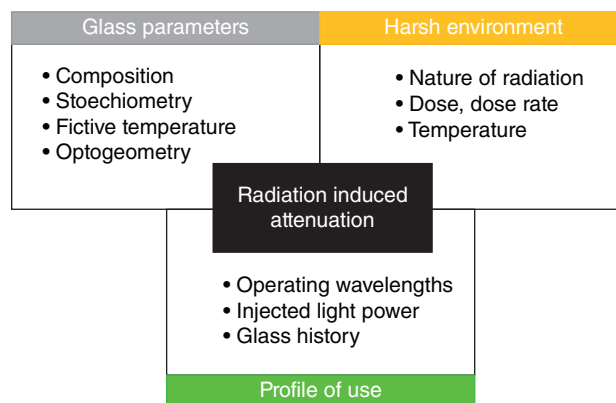


Figure 4 Main intrinsic and extrinsic parameters defining the levels and kinetics of radiation-induced attenuation in optical glasses.

defects having been identified in phosphate glasses [6]. Investigations of alkali silicate, borosilicate, and fluoride glasses have also demonstrated the existence of specific point defects [7, 8]. Among the most important ones are the hole centers associated with B (BOHC), Al (AlOHC), and alkali ions M^+ , for instance, of the HC_1 type: $(\equiv Si-O \dots M^+)$.

The knowledge acquired about point defects allows for a better control of their generation mechanisms and for the development of radiation-hardened optical fibers [9] or optical glasses for lenses. Alternatively, the glass

manufacturing process can also be adapted to favor the generation and stabilization of defects in very sensitive dosimeters. The absorption or luminescence signatures of certain defects are then valuable to monitor large dose ranges or rates. Through its absorption band peaking at 1600 nm in the third telecom window, this is the case of the P_1 defect in phosphorus-doped glasses that makes possible distributed monitoring of doses from a fraction of Gy to 1 kGy(SiO_2) at CERN facilities.

3 Vitreous Phase Stability and Bubble Formation

3.1 Ionizing Irradiation

Two kinds of experimental approaches are followed depending on the electron energy and flux, and thus, on the dose to which a bulk glass is exposed. A dose as high as 1 GGy can be delivered in less than one minute by high-energy electrons in the 100 keV to 1 MeV range by a transmission electron microscope (TEM, cf. Chapter 2.3) but in one day by accelerators. The formation of oxygen bubbles is one of the major features observed under the high-flux irradiation conditions under TEM. Their nucleation and growth are controlled by the electron-beam flux and the irradiation temperature affecting the local glass structure, respectively, and by a breaking of bonds that enhance the diffusion mechanisms of alkali and oxygen atoms [10–12]. In other words, the intense ionization induced by a high electron flux likely causes an effective viscosity decrease due to bond-breaking processes, which in turn enhances alkali and oxygen diffusion and drives phase separation [13]. Through inter- and intra-atomic Auger de-excitation, electron-stimulated desorption (ESD) of alkali, oxygen, and silicon atoms or ions is another important mechanism that can modify local chemical compositions [14] and induce phase transformations. In borosilicate glasses (Chapter 7.6), phase separation, for instance, originates in the depletion of charge-compensating alkali cations and subsequent boron-coordination changes from 4 to 3 [12].

The integrated doses obtained under gamma rays with ^{60}Co or ^{137}Cs sources emitting at energies of 1.17 and 1.33 or 0.66 MeV, respectively, are generally of the order of 1 MGy. In a TEM study of γ -irradiated Na silicate glass, the formation of bubbles was observed, which was attributed to a radiolytic decomposition involving free sodium ions and molecular oxygen [15]. However, no bubbles were detected in a γ -irradiation study of the same glass, even at higher doses [16]. This disagreement illustrates the complexity of understanding the glass response and sheds light on the influence of the characterization of the γ -irradiated glass by TEM that can affect the global response depending on the conditions used

(electron-beam current, magnification and focus, time of electron-beam exposure, etc.).

Finally, lower-energy electrons in the keV range are produced in scanning electron microscopes (SEMs, Chapter 2.3) or electron microprobes (Chapter 5.1). But a major drawback then is the buildup of a negative-charge space caused by the stopping of primary electrons within the sample [10]. In turn, this effect translates into significant field-assisted alkali migration, i.e. in accumulation of alkalis where electrons are implanted and in depletion at the surface. Such modifications of the local glass composition make it necessary to consider the results obtained with care as they may interfere with the irradiation effects themselves.

3.2 Nuclear Collisions

The effects of nuclear collisions have mainly been studied in nuclear glasses either doped with short half-life actinides or bombarded by heavy ions. Of particular interest is the fact that actinide-doped borosilicate glasses do not undergo any phase separation or crystallization detectable by optical microscopy, SEM, and TEM upon exposure up to $10^{19} \alpha/\text{g}$, which would represent the dose received by a waste-storing glass over several hundred thousand years [17]. Likewise, no phase transformations have been observed upon external irradiations of oxide glasses with heavy ions, the only effects being the modifications of the glass structure described in Section 4.1.

For α decay, the possible formation of helium bubbles in actinide-doped glasses has also been studied from a combination of He infusion (i.e. equilibrium at defined T and P between helium gas and a solid) and He-ion implantation experiments along with in-pile irradiation with the $^{10}\text{B}(n, \alpha)^7\text{Li}$ reaction. The result is that bubbles can form when the number of He atoms exceeds that of the sites where they may fit [17], which represents a concentration of about 1–3 at % in borosilicate glasses [18].

4 Glass Network Evolution Under Irradiation

4.1 Structural Effects

Short-range order is very stable in silica glass, which means that Si remains fourfold coordinated regardless of the irradiation conditions [19]. In molecular dynamics simulations, the existence of some fivefold coordinated silicon atoms resulting from displacement cascades has nonetheless been reported [20]. Irradiation, however, affects medium-range order through modifications of angular distributions and ring statistics. In silica glass, a decrease of the Si–O–Si angle and an increase of the Si–O–Si angle distribution can be deduced from the shift

and broadening of the R-band in the Raman spectrum, respectively. The maximum observed decrease of -10° (angle of $\sim 135^\circ$) was obtained after neutron irradiation [19]. The ring statistics is also modified with an enlarged distribution in the irradiated glasses. These glasses contain more small-membered rings, as indicated by the increase of intensity of the D_1 and D_2 Raman bands and from molecular dynamics simulations results obtained on the effects of nuclear collisions [19, 20].

The structural evolution strongly depends on glass composition. In borosilicate glasses, for example, changes of boron and aluminum coordination from 4 to 3 and from 5 or 6, respectively, take place under irradiation as a result of either electronic or nuclear collisions [7, 17]. For both initially fourfold coordinated B^{3+} and Al^{3+} atoms, these coordination changes are due to destabilization of alkali charge-compensating cations, an effect likely associated with alkali migration under irradiation. The formerly charge-compensating alkalis then become network modifiers. They induce a decrease of the glass polymerization index unless they form clusters with other available alkali in their neighborhood, in which case the polymerization index can increase. Hence, the polymerization state of the glass can decrease or increase depending on glass composition and on the type of radiation–matter interaction involved.

Although modifications of local- and medium-range orders upon irradiation are certainly connected, no model currently accounts for the observed structural transformations and predicts their variations with composition. The effects of nuclear collisions have been more extensively studied in the last decade. The results obtained have suggested that the driver of the structural evolutions in both local- and medium-range orders could be associated with a local melting process in the displacements cascade zone, followed by a very high quenching rate step that freezes the glass structure in a higher enthalpy state. Therefore, a model of irradiation-induced vitrification involving ballistic disordering and fast quenching events has been proposed [21] (also called super-vitrification). It also explains the increase of the fictive temperature of the glass observed upon irradiation in a ^{244}Cm -doped borosilicate glass [22].

4.2 Density Effects

Compaction of silica glass under neutron irradiation was first reported in 1958 [23]. The density rate increase is first rapid and saturates with a maximum densification of about 3 at % (Figure 5). This saturation value is the almost the same for all kinds of irradiation (e.g. ions, neutrons, electrons, or UV photons) [19]. Compared with ionizing radiations, nuclear collisions are much more efficient with a saturation reached at $10^{21} \text{ keV}_{\text{nucl}}/\text{cm}^3$ as opposed to around $6 \times 10^{23} \text{ keV}_{\text{elec}}/\text{cm}^3$ for ionizing

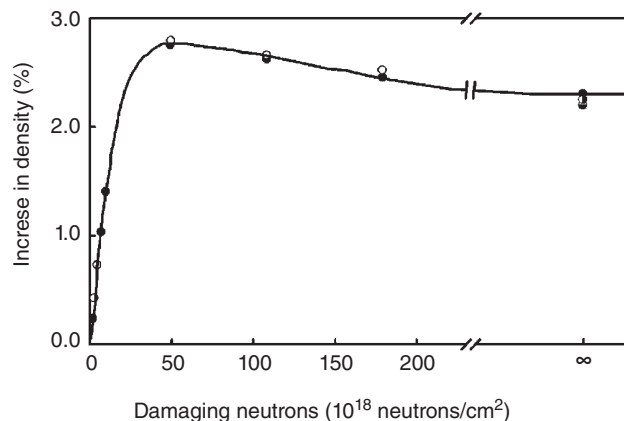


Figure 5 Compaction of silica glass induced by neutron irradiation [22].

radiations [19]. Since high-pressure permanent compaction of SiO_2 glass begins at 9 GPa and reaches 21% at 25 GPa [24], the effects of irradiation are comparatively minor. The dose dependence of compaction obeys a D^n power law where n is $2/3$ for ionizing irradiation and close to 1 in the case of displacement damages [25]. Introduction of hydroxyl groups in pure silica first causes swelling at low doses and then densification. Similar trends are observed for alkali-silicate glasses where the relative contributions of swelling and densification depend on dose and irradiation type (ions or electrons). These more complex trends are due to diffusion of alkali ions under irradiation.

In borate systems, network compaction depends on glass composition and reaches up to a few percent as observed under a flux of neutron or gamma rays (kGy). It is caused by ring rearrangements induced by bond breaking between trigonal groups [26]. In borosilicate glasses, the density change seems to be controlled by the aforementioned structural changes mainly associated with lower boron coordination numbers and an increase of the fraction of non-bridging oxygens. Depending on glass composition, the density can either decrease or increase with irradiation but these variations are always lower than 3 at % [16, 17]. Like SiO_2 glass, compositions with low alkali content tend to shrink upon irradiation whereas glasses with a high alkali content in contrast tend to swell [16].

5 Optical Properties

6 RIA and Emission

As commonly observed, glass darkening or coloration is a striking example of RIA phenomena (Figure 6). As most of the defects absorb at high energies, the decrease of light transmission is usually larger at smaller wavelength, then

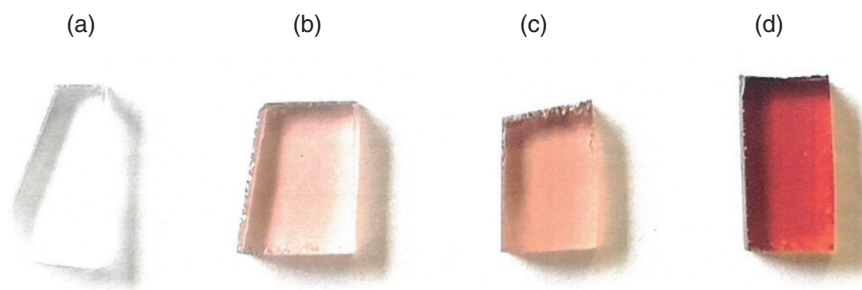


Figure 6 Radiation-induced attenuation in three samples of a fluorophosphate glass (S-FPL51 from OHARA) after irradiation with 6 MeV electrons at room temperature: (a) starting glass; (b) 600 Gy(SiO_2) dose; (c) 1 kGy(SiO_2); and (d) 5 kGy(SiO_2).

very large in the ultraviolet and visible domains (200–700 nm), and lower in the near-infrared range (700–2000 nm) [9]. A second noteworthy effect is the radiation-induced emission of light observed as scintillation of the glass, which of course degrades the signal-to-noise ratio. The emission originates either in particular from point defects (usually in the UV or visible domain) or from Cherenkov radiation (with an intensity peaking near 400 nm and then decreasing at higher wavelengths) [9]. This parasitic light is usually more intense at higher dose rates, and it is generally observed in glasses exhibiting low-to-moderate RIA.

Finally, radiations can induce build-in of charges in the glass, particularly under electron irradiation, initiating dielectric breakdown (Lichtenberg trees) and critical failure of the device. RIA is the limiting parameter in most applications of optical glasses and most optical fibers [9], obviously increasing in the visible domain with the accumulated dose (Figure 6). In practice, this phenomenon and its kinetics are not readily accounted for because they depend on both dose and dose rate, as well as temperature and the radiation type and energy. From the limited data sets available at high dose rates, however, empirical or semiempirical models have been set up to predict RIA as a function of dose and dose rate [9] that are currently used to estimate the vulnerability of fiber optics for space missions.

6.1 Refractive Index

When a large fluence of particles induces displacement damages, any densification is accompanied by changes in the internal stress, polarizability, and refractive index of the glass (Δn is in the 5×10^{-3} to 10^{-2} range for silica [19]). The effect on the last parameter is particularly impactful to optical systems in which it causes lens defocusing. It is also becoming a major issue when it affects the quality of the measurements and the spatial discrimination between events monitored with distributed fiber-based sensors relying on reflectometry techniques. This is particularly the case when environmental parameters, such as temperature and strain, are monitored under harsh environments through their impact of glass scattering signatures.

6.2 RE-Doped Glasses

Oxide glasses doped with trivalent RE ions are of prime importance as active and inactive components in optical and photonic devices, such as lasers or scintillators and phosphors. In these applications, the main irradiation effects are redox changes of the RE. When exposed to γ and X rays or electrons, the stable Eu^{2+} , Yb^{2+} , or Sm^{2+} states can, for instance, readily be formed by electron trapping in silicate, borate, fluorophosphate, or phosphate glasses, whereas Tb^{3+} and Ce^{3+} can be oxidized into Tb^{4+} and Ce^{4+} [27]. Under usual conditions, both Ce^{3+} and Ce^{4+} coexist in glasses where they act as traps of holes and electrons, respectively, limiting in this way the number of absorbing color centers. This is the reason why cerium is often introduced in glasses for limiting radiation effects on optical properties. Actually, doping with REs not only tends to reduce the number of radiation-induced point defects but also to modify the nature of point defects [28]. Unusual divalent states such as Er^{2+} or Nd^{2+} can also be stabilized when a hole center forms in the vicinity of the RE^{2+} . In association with an aluminum-oxygen hole center (OHC), Er^{2+} or Yb^{2+} ions then give rise to the optical-fiber photodarkening [29].

Another effect is the modification of the local environment of the RE (Yb^{3+} , Dy^{3+} , and Eu^{3+}). At doses higher than 10^4 Gy, it manifests itself as a decrease of the site symmetry for Eu^{3+} in different glassy matrices. Along with redox changes, such modifications of the local environment of RE ions cause variations of optical absorption and emission spectra (Chapter 6.2). In addition, the formation of point defects results in increases of the values of optical band gap and of the Urbach energy (i.e. the band absorption edge).

As for the lifetime of the excited states of RE ions, they are generally reduced under irradiation by up to 40% for doses higher than 10^8 Gy. This decrease is not a linear function of the dose as indicated by experiments performed with doses ranging from 100 to 10^9 Gy on glasses doped with Yb^{3+} and Er^{3+} , for which the lifetimes display a “plateau” between 10^5 and 5×10^6 Gy (Figure 7). Interestingly, the dependence of the lifetime on the logarithm of the dose is the same for trivalent RE ions and for phosphate, silica, or aluminosilicate glass matrices [28]. The presence of RE clusters in the glass does impact the

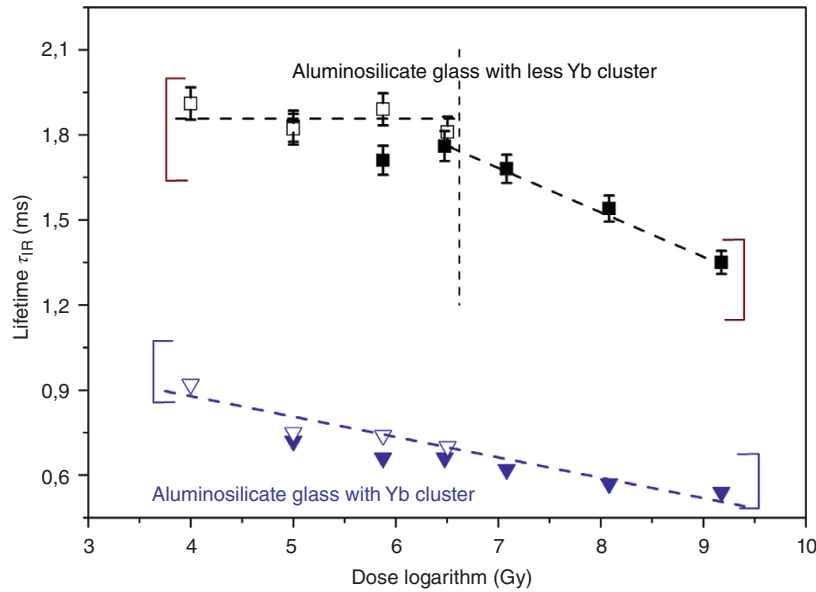


Figure 7 Effects of the radiation dose and Yb clusters on the $^2F_{5/2}$ lifetime of Yb^{3+} for two aluminosilicate glasses (Source: Modified from [27]).

lifetime of excited state (see Figure 7) in connection with the formation of point defects [28].

7 Effect on Mechanical Properties

It is mainly in the context of nuclear-waste vitrification that the effects of radiation on the density and mechanical properties of oxide glasses have been studied. The goal was to evaluate how radiation could affect fracturing of borosilicate glasses subjected to mechanical stresses through measurements of density, hardness, Young modulus, and fracture toughness. Most researches have addressed the influence of alpha decay, which is the main cause of atomic displacements in glass structures under disposal conditions. They have in addition tried to evaluate the respective roles of alpha particles and heavy recoil nuclei through external irradiation with light and heavy ions but also through thermal-neutron irradiation [16, 17]. Fewer studies have addressed the effects of beta decay through electron irradiation [7, 30].

A decrease in hardness and Young modulus, along with an increase in fracture toughness, is always observed. The hardness changes under heavy-ion irradiations are very similar regardless of the glass complexity in borosilicate systems [31], which suggests that they are controlled by the response of the borosilicate network itself. As a function of the irradiation dose, they follow exponential laws with a saturation at deposited energies of 30 MGy and

3 GGy by nuclear and electronic collisions, respectively [32]. Whereas collisions with nuclei are, therefore, about 100 times more efficient than with electrons, the hardness changes induced by the former are approximately twice greater than by the latter at electronic stopping powers lower than 2 keV/nm.

In alpha decay, both nuclear and electronic collisions occur simultaneously through the slowdown of the α particle and the recoiling nucleus. From experiments made under a wide variety of irradiation conditions, it appears that the accumulation of nuclear damage controls the hardness–dose relationship in oxide glasses subjected to alpha decay accumulation [17]. But the picture has been somewhat clarified by dual-beam irradiation experiments made with He and Au ions to study in more detail the synergistic effects of α particles and recoil nuclei on the extent of damage [32]. From sequential and simultaneous ion irradiation, the conclusion drawn is that the electronic energy losses of the α particles induce partial repair of the damage generated by the heavy ions. In other words, the state of the damaged glass is controlled by the mutual interactions between α particles and recoil nuclei.

In microscopic terms, a complementary picture has been brought by molecular dynamics simulations of the indentation of a rapidly quenched disordered sodium borosilicate glass [33]. Under these conditions, the increase of the free volume and the decrease of the polymerization index are the main factors accounting for the hardness decrease of the glass.

8 Mitigation of Radiation Effects

Hydrogen plays a key role in the glass radiation response as it easily interacts with point defects. Hydrogen effects on optical glasses have been thoroughly studied [34] because H_2 loading of germanosilicate optical fibers greatly increases their photosensitivity to ultraviolet laser light, opening the way to the manufacturing of Fiber Bragg gratings. Under irradiation, a glass containing H_2 molecules usually presents a lower radiation sensitivity because hydrogen passivates most of the radiation-induced defects such as the SiE' or non-bridging hole centers [5]. However, it should be considered that the H_2 loading also presents adverse effects such as an increase of the linear attenuation at telecom wavelengths. Furthermore, this hardening technique is difficult to implement for fiber-based systems having to operate during long periods such as in space mission or nuclear industry as the gas easily diffuses out the fiber. Today, no optical glass or optical fiber can be considered as radiation hardened for all harsh environments, even if solutions exist for most of the currently targeted applications [9].

For lenses, most studies have been devoted to glass hardening under conditions relevant to space and those encountered at CERN, which means moderate doses typically not exceeding 100 kGy. In this case, co-doping of glasses with cerium strongly reduces the RIA levels [27], thanks to the incorporation of this element in the silica network as Ce^{3+} or Ce^{4+} ions: as already noted, upon irradiation, Ce^{3+} ions trap the released holes to form $(Ce^{3+})^+$ centers, which inhibit the formation of other trapped hole centers, whereas Ce^{4+} ions trap electrons, which reduces the formation of all centers due to trapped electrons. The relative abundances of both species strongly depend on the redox conditions of manufacturing process. These mechanisms may have a very positive effect on the levels of RIA in the visible so that radiation-hardened glasses are commercially available, with a transmittance edge shifted to longer wavelengths by the absorption of Ce^{3+} and Ce^{4+} ions around 320 and 260 nm. These cover a sufficient part of the Abbe diagram (Chapter 6.1) to make the design of performance optical systems possible for low-to-moderate dose environments. These Ce-bearing glasses are prone to dielectric breakdown, however, so that specific mitigation techniques, such as the addition of protective conductive layers, have to be applied to reduce this risk.

With Ce-co-doping, the radiation sensitivity of silica-based optical fibers has been reduced enough to open the way for a new generation of radiation-tolerant fiber lasers and amplifiers for the most challenging space missions [9]. Finally, Ce-doped silica-based fibers serve as very efficient dosimeters because the luminescence

intensity of Ce^{3+} ions at around 460 nm depends linearly on the dose rate. If the irradiation duration is known, the dose can then be calculated precisely.

Another approach might rely on the mixed alkali effect (Chapter 4.6) to slow down diffusion through mixing of alkalis in the glass composition [35]. In a series of five borosilicate glasses, the structural modifications of the glass network induced by electron irradiation are reduced by a slowdown of the migration of alkali charge-compensating cations for fourfold coordinated B^{3+} in mixed Na, K samples whereas the motion of modifier ions is reduced in Na, Li samples. In this way, the mixed alkali effect also affects boron speciation, i.e. BO_3/BO_4 ratios and, thus, the polymerization index. In addition, it can also act positively by limiting the concentration of point defects when both alkali ions are introduced in equal part in the glass.

Finally, the fictive temperature T_f may also be a parameter relevant to improve the radiation resistance of the glass. In silica, the density increases with T_f via a higher proportion of three- and four-membered rings, which yield a more strained structure. Correlatively, the concentrations of the SiE' , non-bridging oxygen hole center (NBOHC), and self-trapped hole (STH) point defects (Figure 3) increase [36]. Because the E' center and STH point defect contribute the most to optical absorption spectra, monitoring the fictive temperature can be beneficial to decrease the RIA of the fiber and, thus, to optimize its radiation hardness.

9 Perspectives

Even though much knowledge has been acquired in the last 50 years about radiation effects on glasses, several challenges remain to be overcome. First, the contribution of multiscale modeling must be increased, thanks to the development of new simulation tools and to advances in high-performance computing. It will become possible to consider more complex glass structures, to increase the size of the simulation cell, and to deal with the role of impurities so as to reproduce changes in local- to medium-range order. Second, more highly functionalized glasses or optical fibers (e.g. doped sol-gel materials [Chapter 8.2], doping with nanoparticles) will be developed to address new needs in terms of performance in sensing, medicine, or energy sectors. Those new glasses may be used in radiation environment for multiparameter sensing or for dosimetry in the future after having demonstrated their potential in civil applications. Third, new radiation environments will have to be considered either in space or on Earth in facilities devoted to research on nuclear fusion (LMJ, ITER, or DEMO) for which the vulnerability of

glasses and optical fibers will have to be evaluated and radiation hardening studies conducted to ensure their operability. Some of the technical challenges will not be easy to sustain; for instance, the combined radiation and temperature constraints associated with the space missions to the moons of Jupiter or with the in-core monitoring of the next generation of nuclear reactors with temperatures ranging up to 1000 °C. For a given glass and harsh environment, the radiation response will also be driven by the chosen operation profile for the application: operating wavelength(s), the injected light power level, and pre- or posttreatments [9].

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3.14

Amorphous Ices

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1 Introduction

Despite its chemical simplicity, water is one of the most complex substances known as exemplified by unusual properties such as a density maximum near 4 °C, a negative volume of melting, and, thus, freezing temperatures decreasing with increasing pressure. As for the solid phases of water, they are also remarkable in view of the existence of at least 15 ice polymorphs [1]. These original aspects of water largely originate in a contrast between strongly covalent intramolecular H–O bonds and weaker intermolecular bonds between the lone electron pair of the oxygen of a given molecule and the hydrogens of two other molecules. Understanding how a complex interplay of these bonding features results in the unusual properties of H₂O is of a more than purely academic interest because water typically constitutes 80 wt % of living organism and covers 70 % of the Earth's surface. With its vapor in the atmosphere and the large ice caps found around the poles, water is in fact the only important substance naturally occurring so close to its triple point.

The picture of water phases and properties is still more complex because it must also include amorphous ices and their own peculiarities. Although liquid water does not vitrify upon continuous cooling, an amorphous form of ice was first obtained in 1935 by vapor deposition on a copper surface kept below –110 °C [2]. It has been termed low-density amorphous (LDA) ice in view of its room-pressure density of 0.94 g/cm³, which is close to the 0.92 g/cm³ of ice I. This amorphous ice may form in the coldest regions of the Earth's atmosphere, such as the summer polar mesosphere, and might be the most

common form of water in the whole universe either as vapor-deposited thin films onto solid surfaces or as confined in nanometric pores of interstellar matter [3].

Half a century after the synthesis of LDA, another amorphous water phase was obtained below 140 K through uniaxial compression of either hexagonal ice or of the LDA phase at pressures higher than 1.6 GPa (Figure 1) or 0.5 GPa, respectively (Chapter 3.10, [4]). Because of its room-pressure density of 1.17 g/cm³ at 77 K, this phase has been called high-density amorphous (HDA) ice (Figure 1). Further work then showed that HDA ice transforms itself into a third amorphous phase if brought between 1 and 2 GPa at 160 K [5]. Its room-pressure density of 1.26 g/cm³ at 77 K has led this third phase to be discovered at 125 K under 0.95 GPa and termed very high-density amorphous (VHDA) ice [6].

Probably, the most important consequence of these unexpected discoveries was to raise the issue of *polyamorphism*, i.e. of first-order transitions between amorphous phases, and, in turn, of the relevance of this concept to oxide and other glass-forming systems. Because this important topic is dealt with in Chapter 3.9, the focus will be out here to the original amorphous ices and to the way in which their mutual relationships can be understood thermodynamically.

For this purpose, the origin of ice polyamorphism will be rooted in a first-order phase transition between two distinct liquid phases [7], which nucleates homogeneously at different temperatures upon cooling [8]. After a review of the synthesis of these phases and of their thermochemical properties, a simple thermodynamic model will be set up to account for their coexistence curve in the *P,T* plane. The structural significance of these results and their extension to glass-forming liquids, in general, will then be pointed out, attention being in particular paid to glacial phases and ultrastable glasses whose existence is related to polyamorphism. Both have much lower

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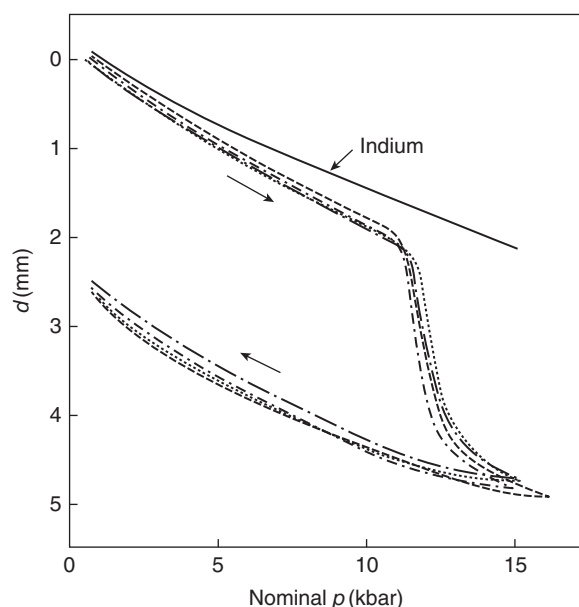


Figure 1 First-order transformation of hexagonal ice into the high-density amorphous phase at 77 K: volume changes as a function of pressure as signaled by the piston displacement in uniaxial compression experiments. *Source:* Reproduced with permission from [4], © Nature Group Publishing.

enthalpies than glasses obtained by melt cooling because the former result from isothermal annealing above T_g [9] and the latter are currently produced by vapor deposition below T_g [10]. Finally, a comparison will be made between H_2O and SiO_2 because of their structural similarities that have long been noticed [11].

Acronyms

HDA	high-density amorphous
LDA	low-density amorphous
LLPT	liquid-to-liquid phase transition
VHDA	very high-density amorphous
VHDL	very high-density liquid
VFT	Vogel–Fulcher–Tammann

2 Ice Phase Transitions

2.1 Calorimetric Observations

All other things being equal, the probability of forming a crystal nucleus in a supercooled liquid is proportional to the size of the sample. For water, the highest degrees of supercooling of 40 K have thus been achieved for capillary samples. Upon cooling, the heat capacity of these samples strongly increases down to 235 K before crystallization takes place and prevents the glass transition from being

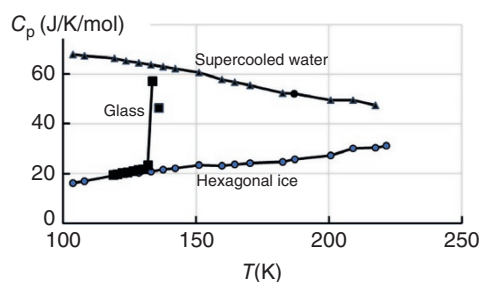


Figure 2 Low-temperature heat capacity of H_2O phases measured upon heating: hexagonal ice, supercooled liquid, and low-density amorphous ice undergoing a glass transition at 133.6 K [14]. *Source:* Reproduced with permission and adapted from [8], © Elsevier.

observed as a rapid C_p decrease [12, 13]. In contrast (Figure 2), a C_p increase typical of a glass transition was observed in 1968 at 133 K upon heating of the LDA ice before its onset of crystallization [14]. As characterized by a C_p rise of more than 35 J/K/mol, this glass transition near 134 K is followed by a sharp exothermic crystallization peak of 1.64 kJ/mol. Interestingly, the C_p peak of the supercooled liquid almost matches theoretically evaluated values [8], whereas the heat capacities of the LDA, hexagonal, and cubic ices are nearly the same below 134 K as may be expected from their purely vibrational nature.

Other relevant measurements have been made on H_2O phases enclosed into nanopores, but the contribution of interfacial water must then be removed as done for ice and emulsified water from the results obtained for pores of variable diameters [15, 16]. In 3 nm pores (Figures 3 and 4), water supercools readily and shows not only a C_p peak at 228 K [15] but also two apparent glass transitions at around 135 and 174 K [16]. In the absence of latent heat, a first-order transition at 228 K was not

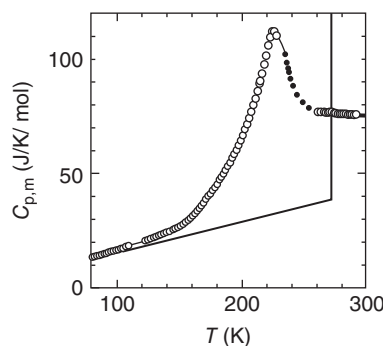


Figure 3 Heat capacity of confined water measured upon heating after elimination of the contributions of interfacial water and of the ice confined within the 3 nm pores of silica gel. Solid circles, emulsified water; solid line, ice. *Source:* Reproduced with permission from [15], © AIP Publishing.

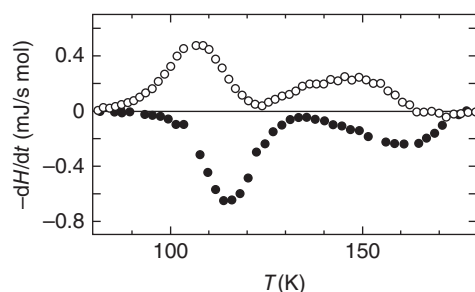


Figure 4 The two glass transitions of amorphous water in calorimetric measurements made on samples enclosed in nanopores 3 nm in diameter: rates of spontaneous heat release and absorption, observed by an intermittent heating method. Open and solid circles: samples cooled before the measurements rapidly at around 5 K/min and slowly at 10 mK/min, respectively. Source: Reproduced with permission from [16] © John Wiley and Sons.

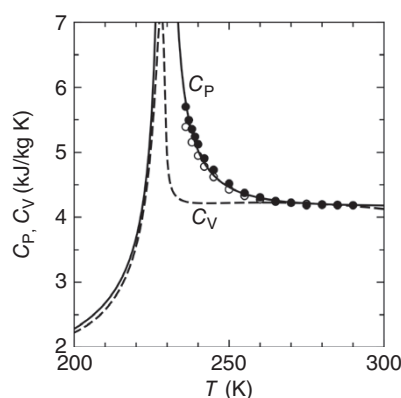


Figure 5 Heat capacity around the onset of ice crystallization near 235 K [13]. Two-state model predictions (curves). Source: Graph courtesy M.-A. Anisimov.

clearly established, but the strong C_p peak of 112 J/K/mol at 227 K is suggestive of its existence. Such a phase transformation is indeed predicted at around 227 K by a two-state model [13, 17, 18], which also accounts well for the heat capacity of supercooled water measured above 235 K (Figure 5).

Together with the two glass transitions, the onset of ice crystallization at 235 and 135 K points to the existence of two distinct supercooled liquids of different densities between which there is a transition at around $T_{LL} = 228$ K at room pressure. This point belongs to a first-order transition curve $T_{LL}(P)$ in the P, T plane that terminates at a critical point [13, 17, 18]. This curve could thus delineate the stability limits of two supramolecular arrangements of hydrogen bonds in water and, also, induce at the same time a transformation from a fragile to a strong liquid (Chapter 3.8) as suggested in 1999

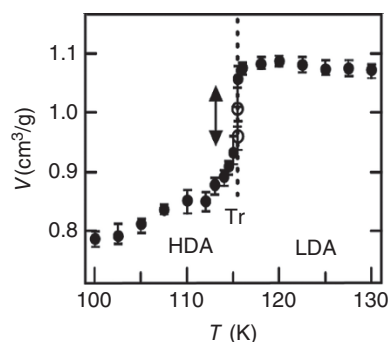


Figure 6 Isothermal volume relaxation over 3 hour durations during the transition from high- to low-density amorphous ice. Source: Reproduced with permission from [5], © Nature Publishing Group.

[19]. But its determination is made difficult by the fact that it is located within the first crystallization zone.

2.2 Phase and Volume Observations

As already noted (Figure 1), hexagonal ice transforms under pressure to the HDA phase at 77 K through a first-order transition [4]. In turn, HDA ice transforms at room pressure into the LDA phase upon isothermal annealing with a volume discontinuity at 116 K of about $0.12 \text{ cm}^3/\text{g}$ (Figure 6) and a volume change of about $0.3 \text{ cm}^3/\text{g}$ between 100 and 116 K [5]. The HDA–LDA ice transition must actually be viewed also as a univariant equilibrium curve in the P, T plane, which may be determined from the volume discontinuities observed as a function of both parameters (Figure 7). Interestingly, this volume change remains basically constant with a value of about $0.2 \text{ cm}^3/\text{g}$ [7], which is smaller than the aforementioned $0.3 \text{ cm}^3/\text{g}$.

Despite their density differences, LDA and HDA ices have similar X-ray diffraction patterns typical of amorphous phases with the expected shift toward shorter interatomic distances in the latter phase as compared with the former (Figure 8) [20]. Interestingly, their formation at around 0.45 and 0.95 GPa, respectively, depends on the compression rate in isothermal experiments performed at 125 K (Figure 9). The excess density at 0.95 GPa is quenched after decompression and leads to an additional volume reduction of $0.3 - 0.2 = 0.1 \text{ cm}^3/\text{g}$. The associated excess enthalpy relaxes and decreases with temperature until the LDA phase enthalpy is reached.

The density of supercooled water above 200 K has been calculated as a function of temperature and pressure with another two-liquid state model. The line of maximum density and that of a constant low-density water fraction

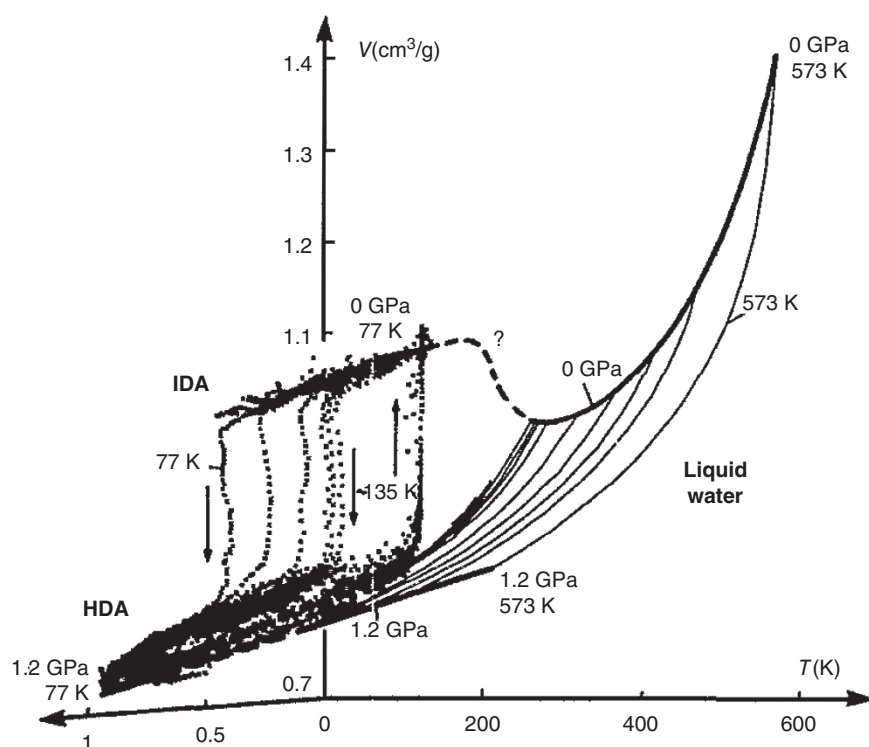


Figure 7 Volume changes as a function of pressure and temperature for the transition between the high- and low-density amorphous ices under nominal pressure of 0.55, 0.45, 0.38, and 0.32 GPa at 77, 100, 121, and 135 K respectively. Liquid water under 1.2 GPa at zero pressure also represented versus temperature. Connection between LDA and liquid state at zero pressure (e.g. liquid 1) occurring at 227 K. *Source:* Reproduced with permission from [7], © AIP Publishing.

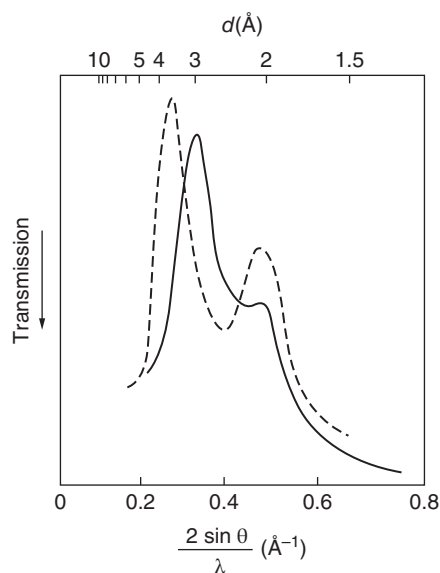


Figure 8 Structural similarities of the low- and high-density amorphous ices seen in X-ray diffraction patterns (micrometer tracing) recorded at room pressure and ~95 K as a function of the scattering angle 2θ at the X-ray wavelength Λ . *Source:* Reproduced with permission from [20], © Nature Publishing Group.

of about 0.12 have also been determined. The existence of a critical point at 227 K at 0.018 GPa is still proposed because of a very strong temperature dependence of the density variation at low pressures [13]. Finally, a minimum of the isothermal compressibility is observed at

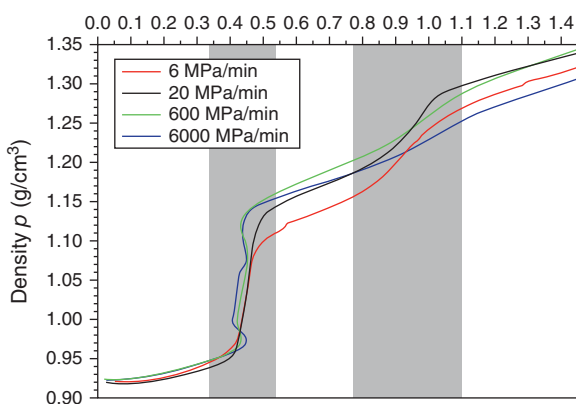


Figure 9 Effect of the compression rate on pressure–density curves for isothermal compression of low-density amorphous ice at 125 K. *Source:* Reprinted with permission from [6], © APS.

318 K [21, 22], which is also accounted for by a two-liquid model [17].

3 Predictions of Glass–Glass and Liquid–Liquid Transitions

3.1 Preliminary Remarks

The starting point of the present thermodynamic analysis of amorphous ices in terms of two initial liquid phases is classical nucleation theory [23] as complemented for each liquid by an additional enthalpy term to predict the

existence of two distinct homogeneous nucleation temperatures T_{n-} and T_{n+} [8, 24]. The nuclei are superclusters, instead of nanocrystals, because these transformations take place in liquids and give rise to usual or ultrastable glasses or glacial phases even to new liquid phases.

Below the melting temperature of ice, T_m , an ordered liquid forms at the lower T_{n-} , i.e. in the no man's land, so it is not easily observed. Above T_m , the higher T_{n+} would signal the onset of superheating as characterized by the disappearance of liquid ordering. For pure liquid elements, one predicts with this model superheating temperatures T_{n+} of $1.198 T_m$ [24, 25] and a Lindemann constant of 0.103. As is well known, Lindemann criterion states that melting occurs when the average relative variations of atomic spacings ($\Delta d/d$) become with increasing temperatures higher than a threshold value, which can be determined from the additional enthalpy term at T_m [26].

The two liquids 1 and 2 have different homogeneous nucleation temperatures, namely, the higher $T_1 = T_n$ and the lower $T_2 = T_g$. The transition at T_g is associated with the reversible enthalpy change from liquid 1 to 2 and by the formation of a glass phase composed of percolating and interpenetrating critical superclusters of the same size in the two ordered liquids whose enthalpies are equal at $T_2 = T_g$.

The glass–glass and liquid–liquid transformations of water under pressure and their latent heats have been predicted [8] from only $T_g \cong 136.6$ K [27], the enthalpy of fusion ($\Delta H_m = 6000$ J/mol), the room-pressure melting temperature of ice ($T_m = 273.1$ K), and the temperature of the compressibility minimum (≈ 318 K) [21, 22]. The transition at T_{LL} is first-order despite the smallness or even the lack of enthalpy discontinuity all along the line $T_{LL}(P)$, which represents a temperature-induced transition from strong to fragile liquid. The high endothermic latent heat expected upon heating is not observed, because it is compensated by the exothermic peak associated with a transformation at 228 K into an ordered liquid called phase 3, which does vitrify below T_g .

Liquids 1 and 2 are fragile above T_{LL} and strong below. They have different homogeneous nucleation temperatures T_1 and $T_2 = T_g$. The glass transition temperature $T_2 = T_g$ of the fragile liquid is lower than T_{LL} but cannot be attained by cooling. As a rule, a strong liquid indeed undergoes a glass transition at the temperature at which the enthalpy difference between the two liquids vanishes, which is higher than that of the fragile liquid.

3.2 Nucleation Temperatures of Ordered Liquid 1 and Ordered Liquid 2

According to classical nucleation theory (Chapter 5.4), the nucleation rate J in a specimen of volume V after a time t is an exponential function of the Gibbs free energy barrier $\Delta G(T)$:

$$J = KVt \exp\left(-\frac{\Delta G}{k_B T}\right), \quad (1)$$

where k_B is Boltzmann constant. A nucleus grows spontaneous in a sample of volume V when J becomes equal to 1 after a time t , which occurs when $\Delta G(T)$ is equal to the critical energy barrier $\Delta G^*(T)$ at the temperature T . Homogeneous nucleation occurs at a temperature T_n in any sample volume V when $\ln K = \Delta G^*/k_B T$, with $\ln K \cong 90$. Liquid ordering induced by the nuclei is expected at this temperature but not observed because crystallization takes place before T_n can be reached. In this model, ΔG includes a negative volume contribution $4\pi R^3/3 \Delta H_m \theta/V_m$ defined by the formation enthalpy of the nucleus at the reduced temperature $\theta = (T - T_m)/T_m$ and a positive surface energy $4\pi R^2 \sigma_1$ depending on the radius R (Chapter 5.4). The critical radius obtained for $d(\Delta G)/dR = 0$ is

$$R_c = -\frac{2\sigma_1 V_m}{(\Delta H_m \theta)}, \quad (2)$$

where σ_1 is the surface energy and V_m is the molar volume. The critical radius is infinite at the temperature of a first-order transition, which is here the melting temperature T_m for $\theta = 0$. The critical energy barrier corresponding to R_c is also infinite for $\theta = 0$. There is no surviving nucleus above T_m because all entities are expected to undergo surface melting at T_m . This classical model neglects the Laplace pressure (ΔP) acting on the nucleus surface, which is proportional to the reciprocal of R . A complementary negative enthalpy $-4\pi R^3 \Delta H_m \varepsilon/3V_m$ must thus be added to ΔG , ε being a fraction of the melting enthalpy ΔH_m . Depending on θ^2 , this term complements the Taylor expansion of the enthalpy Eq. (9) of Chapter 5.4, the derivative $[d(\Delta G)/d\theta]_p$ at T_m remaining equal to the melting entropy $\Delta S_m = \Delta H_m/T_m$ as it must. The new nucleation equation leads to a critical radius proportional to $(1 + \varepsilon)(\theta - \varepsilon)^{-1}$. Large nuclei undergo surface melting, while others melt homogeneously at the reduced temperature $\theta = \varepsilon$ or at higher temperatures depending on whether their size is critical or much smaller than critical [28].

The number of molecules n in a critical nucleus, the two kinds of homogeneous nucleation temperatures θ_{n-} and θ_{n+} , and the thermally activated critical barrier ΔG^* can be calculated as follows [29]:

$$n = -\frac{8N_A k_B (1 + \varepsilon)^3 \ln K}{[27 \Delta S_m (\theta - \varepsilon)^3]}, \quad (3)$$

$$\theta_{n-} = \frac{(\varepsilon - 2)}{3}, \quad (4)$$

$$\theta_{n+} = \varepsilon, \quad (5)$$

$$\frac{\Delta G^*}{(k_B T)} = 12(1 + \varepsilon)^3 \ln \left(\frac{12(1 + \varepsilon)^3 \ln(K \cdot v \cdot t)}{[81(\theta - \varepsilon)^2 (1 + \theta)]} \right). \quad (6)$$

where N_A is the Avogadro number, v the sample volume, t the nucleation time, and ε the fraction of the molar ΔH_m denoted by ε_{ls} for a nucleus in liquid 1, by ε_{gs} for a nucleus in liquid 2, and by $\Delta\varepsilon_{lg} = \varepsilon_{ls} - \varepsilon_{gs}$ for a nucleus of glass phase 3. The parameters ΔH_m and T_m are assumed to be the same for all phases and not to depend on the nucleus radius R . Superclusters spontaneously form by homogeneous nucleation. They are known to have frequently an icosahedral structure (Chapter 2.5). The critical nuclei induce ordering of liquids 1 and 2 below their own homogeneous nucleation temperatures T_1 and T_2 defined by Eqs. (4) and (5). The two ordered liquids transform into glass phase 3 below $T_g = T_2$, which gives rise to various LLPT at new homogeneous nucleation temperatures T_{n+} , according to the thermal variations of $\Delta\varepsilon_{lg} = \varepsilon_{ls} - \varepsilon_{gs}$.

The critical radius and the thermally activated energy barrier are infinite at the homogeneous nucleation temperatures obtained for $\theta_{n+} = \varepsilon$ instead of $\theta = 0$ for the classical equation. Each liquid is ordered at $\theta = \theta_{n-}$. This order disappears upon superheating at $\theta_{n+} = \varepsilon > 0$ but can reappear upon supercooling at $\theta_{n+} = \varepsilon < 0$.

The coefficients ε_{ls} and ε_{gs} represent the critical values of $\varepsilon(\theta)$ in liquids 1 and 2 under pressure. They are related to the homogeneous nucleation temperatures θ_{n-} given by Eq. (4) for ordering formation in liquids 1 and 2 by

$$\varepsilon_{ls}(\theta) = \varepsilon_{ls0} \left(\frac{1 - \theta^2}{\theta_{0m}^2} \right) + \Pi_1, \quad (7)$$

$$\varepsilon_{ls}(\theta) = \varepsilon_{gs0} \left(\frac{1 - \theta^2}{\theta_{0g}^2} \right) + \Pi_2 + \Delta\varepsilon, \quad (8)$$

where P_0 is room pressure and $\Pi_1 = (P - P_0) V_{m1}/\Delta H_m$ and $\Pi_2 = (P - P_0) V_{m2}/\Delta H_m$ are the pressure contributions to the enthalpy coefficients ε_{ls} and ε_{gs} ; $\Delta\varepsilon$ is the latent heat of an existing first-order transition. The dependence of ε on θ^2 has been deduced from the maximum supercooling rate of 30 liquid elements [25]. The coefficients ε_{ls} and ε_{gs} are zero at the reduced temperatures θ_{0m} and θ_{0g} for $\Pi_1 = 0$ and $\Pi_2 = 0$, which correspond to the Vogel–Fulcher–Tammann (VFT) temperatures of the ordered liquids 1 and 2, respectively. The volume of the sample is minimum at the VFT temperature of liquid 1 because T_{0m} is larger than T_{0g} . Combining Eqs. (4) and (8), one obtains a quadratic Eq. (9) whose solutions θ_{n-} for liquid 2 is given by Eq. (10):

$$\varepsilon_{gs0} \theta_{0g}^{-2} \theta_{n-}^2 + 3\theta_{n-} + 2 - \varepsilon_{gs0} - \Pi_2 - \Delta\varepsilon = 0. \quad (9)$$

$$\theta_{n-} = \frac{\left(-3 \pm \left[9 - 4(2 - \varepsilon_{gs0} - \Delta\varepsilon - \Pi_2) \varepsilon_{gs0} / \theta_{0g}^2 \right]^{1/2} \right) \theta_{0g}^2}{(2\varepsilon_{gs0})}, \quad (10)$$

where θ_{n-} of ordered liquid 2 for the sign + is θ_2 .

Likewise, Eqs. (4) and (7) lead to a quadratic equation whose solutions θ_{n-} for liquid 1 are also given by Eq. (10) where $\Delta\varepsilon = 0$ and the subscripts $gs0$ and $0g$ are replaced by $ls0$ and $0m$ and Π_2 by Π_1 , respectively. The transition leading to ordered liquid 1 occurs upon cooling at θ_1 in the no man's land. It could have been first observed upon electrostatic levitation of a metallic melt [30]. The most important phase transition occurs at zero pressure at the homogeneous nucleation temperature θ_2 of ordered liquid 2: by mixing the ordered liquids 1 and 2, it leads to the formation of glass phase 3 characterized by the enthalpy coefficient $\Delta\varepsilon_{lg} = \varepsilon_{ls} - \varepsilon_{gs}$.

Liquid 1 is strong when T_{0m} is smaller than $T_m/3$ ($\theta_{0m} < -2/3$) and fragile when T_{0m} is higher than $T_m/3$ ($\theta_{0m} > -2/3$). These two families have different thermodynamic properties below T_g . In all strong liquids, the coefficients ε_{ls0} in Eq. (7) and ε_{gs0} in Eq. (8), calculated with $\Pi_2 = 0$, $\Pi_1 = 0$, and $\theta_g = \theta_2$, are determined from the known values of θ_2 , θ_{0g} , and θ_{0m} [29]; the glass transition then occurs at the temperature θ_g for which $\varepsilon_{ls} = \varepsilon_{gs}$. In the great majority of strong liquids, (θ_{0g}) is equal to -1 . For all strong glasses for which $\theta_{0m} = -2/3$ and $\theta_{0g} = -1$, the homogeneous nucleation temperatures of liquids 1 and 2 are equal to T_g at zero pressure. With a negative homogeneous nucleation temperature, liquid 1 cannot be ordered for $\theta_{0m} < -2/3$. Nevertheless, a liquid–glass transition still occurs in liquid 2 at a temperature called T_g , where $\Delta\varepsilon_{lg}$ is zero, and is associated with the enthalpy change from liquid 1 to 2. Phase 3 is ordered at $T < T_g$.

Alternatively, a liquid is *fragile* when there is a unique solution to each quadratic equation for Π_1 and $\Pi_2 = 0$. In all fragile liquids, the value of ε_{ls0} minimizing the additional enthalpy given in Eq. (11) is for $\Pi_1 = 0$ and $\theta_1 > \theta_g$:

$$\varepsilon_{ls}(\theta = 0) = \varepsilon_{ls0} + \Pi_1 = 1.5 \times \theta_1 + 2 + \Pi_1 = a \times \theta_g + 2 + \Pi_1, \quad (11)$$

where a is unity in many of them and the reduced temperature (θ_{0m}) respecting Eq. (12):

$$\theta_{0m}^2 = \frac{8}{9} \varepsilon_{ls0} - \frac{4}{9} \varepsilon_{ls0}^2. \quad (12)$$

The additional enthalpy of liquid 2 is minimized with the coefficient ε_{gs0} given by Eq. (13) for $\Pi_2 = 0$ and $\Delta\varepsilon = 0$ [29]:

$$\varepsilon_{gs}(\theta = 0) = \varepsilon_{gs0} + \Pi_2 = 1.5 \times \theta_g + 2 + \Pi_2 + \Delta\varepsilon \quad (13)$$

when Eq. (14) is respected:

$$\theta_{0g}^2 = \frac{8}{9} \varepsilon_{gs0} - \frac{4}{9} \varepsilon_{gs0}^2. \quad (14)$$

The glass transition θ_g of a fragile liquid now occurs at a temperature smaller than that for which $\varepsilon_{ls} = \varepsilon_{gs}$.

3.3 High-Pressure Homogeneous Nucleation of Glass Phase 3

Below θ_g , the difference between the enthalpy coefficient ($\Delta\epsilon_{lg}$) of liquids 1 and 2 given by Eq. (15) under pressure gives rise to the new glass phase 3 instead of ordered liquid 2:

$$\Delta\epsilon_{lg}(\theta) = \epsilon_{ls} - \epsilon_{gs} = \epsilon_{ls0} - \epsilon_{gs0} + \Delta\epsilon + \Pi_1 - \Pi_2 - \theta^2 \left(\epsilon_{ls0}/\theta_{0m}^2 - \epsilon_{gs0}/\theta_{0g}^2 \right), \quad (15)$$

where $\Delta\epsilon$ is here a latent heat or an excess enthalpy frozen in upon quenching. The difference $\Delta\Pi = \Pi_1 - \Pi_2 = \delta V P / \Delta H_m$ is proportional to the volume change δV and to the pressure P at the transition temperature. Then $\Delta\Pi$ is zero for $\delta V = 0$, and T_g remains unchanged under pressure in the absence of latent heat. For a first-order transition, T_g is given by Eq. (10) in which $\Delta\epsilon$ is the latent heat and $\Pi_2 = 0$.

When heated above the glass transition θ_g at zero pressure, the glass phase 3 transforms into the ordered liquid phase 3, which can superheat above T_g and T_m . This liquid “melts” upon heating of the critical superclusters at the reduced temperature $\theta_{n+} > 0$ given by Eq. (3), but it can nucleate again at much lower temperatures from smaller superclusters not melted by overheating ($\theta_{n+} < 0$). In agreement with Eq. (5), one calculates $\theta_{n+} = \Delta\epsilon_{lg}$ with $\Delta\epsilon = 0$ and $(\Pi_1 - \Pi_2) = 0$ from Eq. (15). The nucleation temperature ($\theta_{n+} < 0$) depends on the overheating rate of liquids above T_m and is expected to vanish when all superclusters surviving above T_m have melted.

The melting enthalpy of phase 3 given by Eq. (15) for $\theta = 0$ is $\Delta\epsilon_{lg0} = \epsilon_{ls0} - \epsilon_{gs0}$, which reveals the presence of an underlying first-order transition without latent heat at a temperature T_{K2} at which $\Delta\epsilon_{lg}(\theta)$ and $-\Delta\epsilon_{lg0}$ are equal [24, 31]. The reason why T_{K2} cannot be attained in supercooled water is simply that it is lower than the Kauzmann temperature. The excess enthalpy coefficient at T_m is $-\Delta\epsilon_{lg}(T_K)$ instead of $\Delta\epsilon_{lg0}$.

3.4 Transformation of Phase 3 Under Pressure into a Lower-Enthalpy Glass

The thermally activated energy barrier is defined by Eq. (16) for the transformation of phase 3 [29]:

$$\Delta G^*/(k_B T) = 12(1 + \Delta\epsilon_{lg})^3 \frac{\text{Ln}(K, \nu, t)}{[81(1 + \theta)\Delta\epsilon_{lg}^2]}. \quad (16)$$

The enthalpy of phase 3 varies with P as shown in Eq. (15) and causes $\Delta\epsilon_{lg}$ to vanish before the transformation at the temperature θ_{sg} that depends on $(\Delta\Pi, \Pi_1 - \Pi_2)$. The

enthalpy difference between the HDA and LDA phases after the first-order transition is limited for all pressures by the maximum enthalpy change $\Delta\epsilon_{lg}(\theta_{0m})$ obtained at the VFT temperature $T_{0m} = T_m/3$ of liquid 1 with T_m decreasing under pressure.

The reduced transformation temperature θ_{sg} depends on pressure, because of its initial contribution ($\Delta\Pi_1 = \Pi_1 - \Pi_2$) to Eq. (15), and also on enthalpy at the onset of the first-order transition:

$$\theta_{sg} = - \left[(\epsilon_{ls0} - \epsilon_{gs0} + \Delta E + \Delta\epsilon + \Delta\Pi_1)^{1/2} \left(\frac{\epsilon_{ls0}}{\theta_{0m}^2} - \frac{\epsilon_{gs0}}{\theta_{0g}^2} \right)^{-1/2} \right]. \quad (17)$$

Here a new coefficient ΔE is added because the underlying first-order transition at $T_{sg} = T_K$ fixes the minimum value of $\Delta\epsilon_{lg}(\theta)$ at the Kauzmann temperature instead of $\Delta\epsilon_{lg0}$ at a lower temperatures [24, 31]. This coefficient ΔE affects two temperatures T_{sg} . First, for the HDA phase the parameter $\Delta\epsilon_{lg}$ of Eq. (15) is zero at its T_g calculated with Eq. (10) under the Laplace pressure of a confined space, i.e. $\Pi_1 - \Pi_2 = 0$, $T_m = 273.14$ K, and $\Delta\epsilon = \Delta\epsilon_{lg}(T_{0m})$. Upon annealing at this temperature, this transition to a glacial phase could take place under Laplace pressure [24]. The value of ΔE in Eq. (17) is then determined for $\theta_{sg} = \theta_g$, $\Delta\Pi = 0$, and $\Delta\epsilon = 0$ at the onset of the transition. Second, the underlying first-order transition occurs here at the Kauzmann temperature T_K when $\Delta\epsilon_{lg}$ attains its minimum value $\Delta\epsilon_{lg}(T_K)$. Because there is no entropy left at T_K , this underlying transition also occurs without latent heat, i.e. for $\Delta\epsilon_{lg} = 0$ in Eq. (15), and is accompanied by an enthalpy change $\Delta\epsilon_{lg0} + \Delta E = 2 \Delta\epsilon_{lg}(T_K)$ that leads to an ultrastable glass phase with $\Delta\Pi = -\Delta\epsilon_{lg}(T_K)$ and $\Delta\epsilon = 0$ when $T_{sg} = T_K$. Only the latent heat $\Delta\epsilon_{lg}(T_K)$ of the ultrastable phase can then be recovered at T_g by relaxation because the second part $\Delta\epsilon_{lg}(T_{K2})$ remains an excess enthalpy up to T_m . The Kauzmann temperature of supercooled water is determined from $\Delta\epsilon_{lg0} + \Delta E = 2 \Delta\epsilon_{lg}(T_K)$.

4 Numerical Applications to Water

4.1 Heat Capacity Below T_g at Zero Pressure and Kauzmann Temperature

The reduced temperatures θ_{0g} and θ_{0m} of the strong liquids are -1 and $-2/3$, respectively, because the VFT temperatures are assumed to be 0 K below T_g for liquid 2 and $T_m/3$ for liquid 1. From $T_g = 136.2$ K [27] and $\theta_g = -0.50128$, one calculates ϵ_{ls} , ϵ_{gs} , and their difference $\Delta\epsilon_{lg} = \epsilon_{ls} - \epsilon_{gs}$ with Eqs. (9) and (15) and the coefficients of Table 1.

The specific heat of the supercooled phase 3 is $\Delta H_m d(\Delta\epsilon_{lg})/dT$ (Figure 2). Without imposing any entropy

Table 1 Coefficients involved in the enthalpy of strong and fragile liquids and phase 3 and characteristic temperatures represented in Figure 12.

	No	Strong liquid 1	Strong liquid 2	No	Fragile liquid 1	Fragile liquid 2	No	Strong phase 3	Fragile phase 3
θ_1	9,10	-0.50128			-0.11792				
$\theta_2 = \theta_g$			-0.50128			-0.2081		-0.50128	
ϵ_{ls0}	9	1.1416		11	1.8232				
ϵ_{gs0}	9		0.66278	13		1.68785			
$\Delta\epsilon_{lg0}$							15	0.47893	0.13527
θ_{0m}^2		0.44444		12	0.14333				
θ_{0g}			1	14		0.23416			
$\epsilon_{ls0}/\theta_{0m}^2 - \epsilon_{gs0}/\theta_{0g}^2$								1.90593	5.51206
θ_{Br-}							15	-0.50128	-0.15665
θ_{LL}		-0.15665	-0.15665		-0.15665	-0.15665		-0.15665	-0.15665
$\theta_{n+} < 0$							5,15	-0.30344	-0.09031
$\theta_{n+} > 0$							5,15	0.30344	0.09031
θ_{Br+}							15	0.50128	0.15665
T_{0g} (K)			0			141			
T_{0m} (K)		91.05			169.7				
T_K (K)	15,17	120.43	120.43		120.43	120.43		120.43	120.43
$T_2 = T_g$ (K)			136.22			216.3			
T_{Br-} (K)								136.22	216.3
T_{LL} (K)		230.35	230.35		230.35	230.35		230.35	230.35
T_1 (K)		136.22			240.9				
T_{n+} (K)								190.3	248.5
T_{n+} (K)								356	297.8
T_{Br+} (K)								410	316

constraint induced by the Kauzmann temperature, one finds that the minimum enthalpy coefficient of phase 3 is -0.36816 for $\epsilon_{ls} = 0$ at $\theta = \theta_{0m} = -2/3$ (Figure 10) and that the enthalpy available below T_g is 1640 J/mol from the crystallization enthalpy around T_g [14]. The minimum enthalpy cannot be attained because the crystal enthalpy difference of 1640 J/mol is much smaller than 2209 J/mol (i.e. 0.36816 times 6000). Between 116.7 and 228 K, the entropy change calculated from the theoretical C_p is already $\Delta S_m = 21.967$ J/K mol. The Kauzmann temperature is higher than the previous evaluation of 115.5 K [8], with a value $T_K = 120.4$ K (Section 4.3) associated with a crystallization enthalpy of 0.23364 $\Delta H_m = 1402$ J/mol.

Upon isothermal relaxation from VHDA to LDA ice (Figure 6), the volume changes by about $0.12 \text{ cm}^3/\text{g}$ at 116 K, when $\Delta\epsilon_{lg}$ is zero as predicted by Eq. (17) with an excess enthalpy $\Delta\epsilon = -\Delta\epsilon_{lg} = 0.15188$ and $\Delta\Pi = 0$,

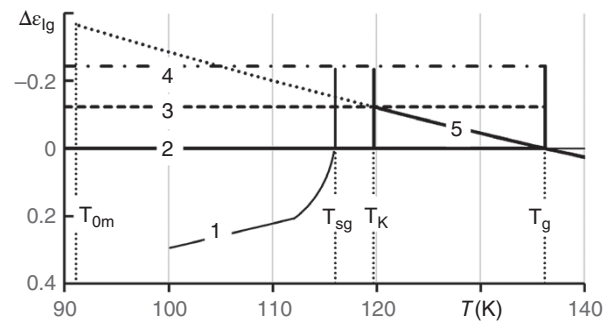


Figure 10 Enthalpy coefficients of supercooled water below T_g . Line 1: relaxation of the enthalpy coefficient $\Delta\epsilon_{lg}$ of phase 3 from VHDA to LDA (corresponding to the volume relaxation in Figure 6). Line 2: $\Delta\epsilon_{lg} = 0$; glass phase 3. Line 3: $\Delta\epsilon_{lg} = -0.11682$; fully relaxed glass phase 3. Line 4: $\Delta\epsilon_{lg} = -0.23364$, ultrastable glass phase 3 down to $T_K = 119.7$ K. Line 5: phase 3 in the absence of the glass transition. For $T = T_{0m} = 91.05$ K, $\Delta\epsilon_{lg} = -0.36816$.

leading to a change in the enthalpy coefficient of 0.23364. In a plot of $\Delta\epsilon_{lg}$ against T (Figure 10, where the axis $\Delta\epsilon_{lg}$ is reversed), this process represented by line 1 leads to the formation of an ultrastable LDA phase 3 on line 4. By comparison, the glass phase is represented by line 2 for $\Delta\epsilon_{lg} = 0$ and the fully relaxed glass by line 3. Sharp transitions at temperatures T_{sg} (where $\Delta\epsilon_{lg} = 0$) toward glasses of lower enthalpy are indeed predicted by Eq. (17) when an excess enthalpy is frozen in upon quenching [24].

The enthalpy coefficient of the fully relaxed glass phase cannot be smaller than its value (-0.11682) at the Kauzmann temperature T_K , whereas that of the ultrastable phase 3 cannot be smaller than -0.23364 . An underlying first-order transition without latent heat occurs at T_K as predicted by theoretical work [31]. In addition, there is no more enthalpy available at T_K for a first-order transition accompanying the formation of the ultrastable phase 3.

4.2 Heat Capacity of Confined Water and the Glass Transition at $T_g = 177.5$ K

According to Young–Laplace equation, $\Delta P = 2\gamma/R = 0.11$ (2) GPa for $R = 1.5$ nm and a surface tension γ of 0.085 (5) J/m² at 227.5 K as extrapolated above 250 K [32]. For $R = 0.55$ nm, ΔP is about 0.30 (4) GPa.

A C_p bump of about 112 J/K mol is observed around 228 K for 3 nm pores (Figure 3). This value is used to fix $a = 0.85$ in Eq. (11) and reproduce the 37.9 J/K mol C_p increase of the fragile phase 3 from T_m to 230.35 K (cf. Section 4.5). Although T_{LL} does not depend on Laplace pressure and T_m still is 273.1 K, the excess

enthalpy $\Delta\epsilon$ relaxes for water confined into 3 nm pores submitted to Laplace pressure (Figure 4). Two apparent transitions are found: in the first, the initial $\Delta\epsilon$ disappears around $T_g = 136$ K, whereas the new $\Delta\epsilon$ does so near 174 K under Laplace pressure. In all HDA ices under critical pressure, T_g is equal to $0.65 T_m$. The same applies to confined water with a T_m of 273.1 K (Figure 4).

4.3 First-Order LDA–HDA Ice Transition Under Pressure

With the parameters of Table 2, the LDA–HDA transition can also be analyzed in terms of an enthalpy excess change occurring at $\theta = \theta_{sg}$ under pressure (Figure 11). The LDA phase 3 has an effective excess $\Delta\epsilon_{eff} = \Delta E + \Delta\Pi_1$ in Eq. 15 ($\Delta\epsilon = 0$) before the occurrence of the transition. This first-order transformation is such that the total enthalpy increase at equilibrium cannot be larger than the maximum enthalpy difference $0.36816 \Delta H_m$ (produced at the VFT temperature $\theta_{0m} = -2/3$) to escape from crystallization. The HDA phase has an enthalpy difference ($\Delta\Pi_2$) with the LDA phase at the temperature T_{sg} after transformation. In all transitions $|\Delta\Pi_2|$ is equal to this maximum value obtained under a pressure of 0.55 GPa: $P \Delta V_2 / \Delta H_m = 0.36816$ with $P = 0.55$ GPa and $\Delta V_2 = -0.22 \times 10^{-6}$ cm³/g.

As discussed in Section 3.4, the temperature $T_{sg} = T_g = 177.5$ K is used to determine ΔE because $\Delta\epsilon_{lg}$ and $\Delta\Pi_1$ are zero at the onset of this transition. With Eq. (17), one then finds $\Delta E = -0.24529$ (Table 2). The Kauzmann temperature is 120.4 K for $\Delta\epsilon_{lg} = (\Delta\epsilon_{lg0} + \Delta E)/2 = 0.11682$, $\Delta\epsilon$, and $\Delta\Pi = (\Pi_1 - \Pi_2) = 0$ in Eq. (15).

Table 2 First-order glass-to-glass transitions under various pressures.

1	P (GPa)	0.55	0.45	0.38	0.32	0
2	T_{sg} (K)	77	100	121	133.3	177.5
3	T_m (K)	152.5	189.5	222.1	240	273.1
4	ΔE	-0.24519	-0.24519	-0.24519	-0.24519	-0.24519
5	$\Delta\Pi_1$	0.23364	0.19116	0.16142	0.13594	0
6	$\Delta\epsilon_{eff}$	0.01135	-0.05403	-0.08377	-0.10925	0.1582
7	θ_{sg}	-0.49515	-0.4721	-0.45528	-0.44035	-0.35013
8	$\Delta\Pi_2$	-0.36816	-0.36816	-0.36816	-0.36816	
9	θ_g	-0.35013	-0.35013	-0.35013	-0.35013	-0.35013

1. Pressure (P); $P = 0$ includes Laplace pressure. 2. First-order transition temperature under pressure P . 3. Pressure-dependent melting temperature. 4. ΔE , enthalpy coefficient excess at T_{sg} . 5. ($\Delta\Pi_1 = P \times \delta V_1 / \Delta H_m$), the change of the enthalpy coefficient associated with the volume difference δV_1 between liquid and glass before the transformation from LDA to HDA under pressure (P). 6. ($\Delta\epsilon_{eff} = \Delta\Pi_1 + \Delta E$); 7. $\theta_{sg} = (T_{sg} - T_m) / T_m$ calculated with Eq. 17. 8. ($\Delta\Pi_2 = P \times \delta V_2 / \Delta H_m$), change of the enthalpy coefficient associated with the volume difference induced by the first-order transition under pressure. 9. ($\theta_g = (T_g - T_m) / T_m$), reduced glass transition temperature of HDA under pressure.

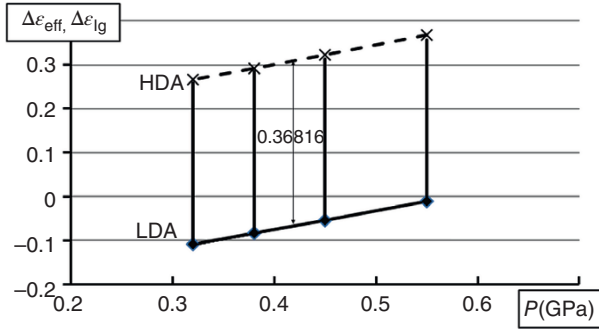


Figure 11 Enthalpy coefficients vs. pressure (P) and sharp enthalpy coefficient changes ($\Delta\epsilon_{lg}$) at $\theta = \theta_{sg}$: HDA line represented by ($\Delta\epsilon_{eff} + 0.36816$) versus P (GPa). Enthalpy coefficient changing ($\Delta\epsilon_{lg} = -0.36816 = \Delta P_2$) on vertical lines. LDA line: calculated points of $\Delta\epsilon_{eff}$ corresponding to Mishima's measurements reproduced in Figure 7 at 77 K and 0.55, 0.45, 0.38, and 0.32 GPa.

In Table 1, $\Delta\epsilon_{eff}$ is calculated with Eq. (17) and $\Delta\epsilon = 0$ at the reduced temperature θ_{sg} , whereas $\Delta\Pi_1$ is proportional to P with $\Delta E = -0.24529$. The melting temperature T_m under pressure is deduced from θ_{sg} and T_{sg} in agreement with the experimental values [33].

A transition at $T_g \cong 180$ K is observed in the heat capacity of all deposited thin films. It can be attributed to a thin layer in contact with the substrate because the latent heat of the first-order transition is very small compared with $0.36816 \Delta H_m = 2209$ J/mol [34].

4.4 VHDA Ice

Following the volume change assigned to the HDA–VHDA transformation observed at 125 K at $P \approx 0.95$ GPa (Figure 9), an additional volume reduction of 0.0855 [6] or $0.1 \text{ cm}^3/\text{g}$ (Figure 6) is observed after decompression at 77 K. In the strong liquid, this transition occurs above T_m when Eq. (3) is respected for $\theta_{n+} = 0.3034$ ($T_{n+} = 1.3034 T_m$) and is accompanied by an endothermic enthalpy of $0.3034 \Delta H_m = 1820$ J/mol. The theoretical volume change $\delta V = 0.3034 \Delta H_m / P = 18 \times 10^{-7} \text{ cm}^3/\text{mol}$ agrees with the experimental results (Figures 6 and 9). At 0.95 GPa, the melting temperature of ice Ih is $125/1.3034 = 96$ K, in agreement with Mishima's measurement [33]. This transformation at 125 K above T_m leads to a VHDL instead of a VHDA phase whose amorphous state is caused by the decompression upon increases of T_m . This first-order transition above T_m represents “melting” of the ordered liquid phase 3. Despite the predictions of Eq. (5), this phase does not nucleate at $\theta_{n+} = \Delta\epsilon_{lg} = -0.3034$ upon decompression because the excess enthalpy has not disappeared. All residual superclusters melt as T_m becomes much lower than 125 K above 1.4 GPa, whereas the lack of a transition induced by residual nuclei causes the additional volume

reduction of $0.1 \text{ cm}^3/\text{g}$ to be frozen in after decompression.

4.5 Fragile-to-Strong Liquid Transformation of Water at Room Pressure

To obtain a weakly endothermic effect upon heating and a glass transition temperature of 136.22 K ($\theta_g = -0.50128$), the temperature of the first-order fragile-to-strong liquid transition of water T_{LL} is taken here as 230.35 K ($\theta_{LL} = -0.15665$). The temperatures T_{Br-} and T_{Br+} (Table 1) are such that $\Delta\epsilon_{lg}$ is 0 in Eq. (16), with $\Delta\epsilon = 0$ and $\Pi_1 = \Pi_2 = 0$, and they cannot depend on P because of the lack of an initial volume difference. In the fragile state, the reduced temperatures $\theta_{LL} = \pm 0.15665$ (i.e. θ_{Br+} and θ_{Br-}) are symmetrical with respect to T_m (Figure 12). Whereas the transition from liquid 1 to liquid 2 is expected at T_{Br-} , there is a compressibility minimum of bulk water for $\Delta\epsilon_{lg} = 0$ above T_m at around 317 K because liquids 2 and 1 have the same enthalpy coefficient [21, 22]. The value $a = 0.85$ in Eq. (11) is used for the fragile liquid 1 and leads to $T_{om} = 169.7$ K, in good agreement with the VFT temperature 168.9 K [35]. The specific heat $d(\Delta\epsilon_{lg})/dT \Delta H_m$ of phase 3 at T_{LL} is taken as 37.6 J/K/mol in agreement with its variation between T_m and 227 K (Figure 3).

The enthalpy of liquid 1 strongly increases upon heating through T_{LL} , whereas that of phase 3 decreases (Figure 12). The two latent heats are nearly equal with opposite signs, their difference at T_{LL} being $1.4 \times 10^{-4} \Delta H_m = +0.84$ J/K mol. Glass phase 3 then transforms into an “ordered” liquid at T_g , which exists up to T_{LL} . A first-order transition without apparent latent heat is consistent with the C_p of confined water (Figure 2), which does not reveal highly critical variations at T_{LL} [15].

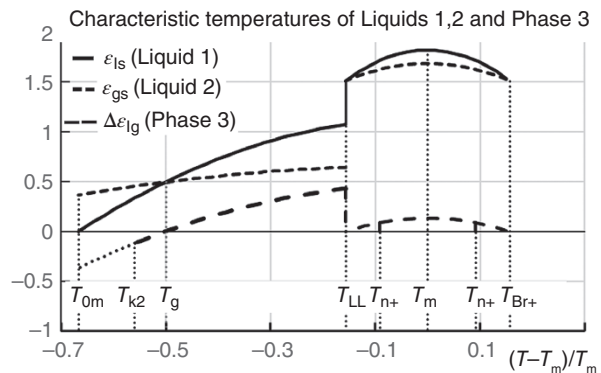


Figure 12 Enthalpy coefficients ϵ_{lg} , ϵ_{gs} , and $\Delta\epsilon_{lg}$ of liquid 1, liquid 2, and phase 3 (see Table 1), $\Pi = 0$. Strong liquid 1 below $\theta_{LL} = -0.15665$ and fragile liquid 1 above θ_{LL} . Characteristic temperatures: $T_{om} = 91.05$ K, $T_{K2} = T_K = 220.4$ K, $T_g = T_{Br-} = 136.22$ K, $T_{LL} = 230.35$ K, $T_{n+} = 248.47$ K, $T_m = 273.14$ K, $T_{n+} = 297.81$ K, $T_{Br+} = 315.93$ K. Source: Reproduced with permission and adapted from [8], © Elsevier.

Phase 3 contributes to the enthalpy change at T_{LL} only when it is ordered after cooling of supercooled water below T_g or $T_{n+} = 190.3$ K, the existence of this transition depending on the rate at which residual water superclusters melt upon overheating.

Upon heating, the model predicts the appearance at T_{LL} of a new fragile and ordered phase 3 existing up to $T_{n+} = 297.8$ K – $\theta_{n+} = 0.09031$ with Eq. (5), which could reappear at 248.5 K after a very moderate overheating above 298 K. But crystallization has until now prevented these predicted supercooled and superheated phases 3 from being observed.

The excess $\Delta\epsilon_{lg0}$ of the fragile phase 3 given by Eq. (15) at $\theta = 0$ is 0.13527 instead of being exactly $\Delta\epsilon_{lg}(T_K) = 0.11682$. The parameters T_{LL} and a in Eq. (11) can be adjusted to obtain a strict equality. The existence of an underlying first-order transition without latent heat is confirmed.

4.6 The Phase Diagram of Water at $-0.175 \leq P \leq 0.176$ GPa

The reduced temperature θ_{LL} does not depend on P despite the proportionality relation $T_{LL} = 0.84335 T_m$. Without changing the values of θ_{LL} and θ_g , pressure simply induces a vertical translation of all points $\Delta\epsilon_{lg} = 0$ in Figure 12. The enthalpy coefficients of fragile liquids at T_{LL} cannot be higher than 2. Consequently, the first-order transition at T_{LL} exists up to a pressure $P \approx 0.176$ GPa corresponding to $\Pi_1 = \Pi_2 = 0.49003$ and a density $\rho = 1.08$ g/cm³. In the phase diagram of supercooled water (Figure 13), the homogeneous nucleation temperatures θ_2 and θ_1 of the strong liquids 2 and 1 are calculated as a function of Π_2 and Π_1 with Eq. (10) for $\Delta\epsilon = 0$: they are higher than the thermodynamic transition at $\theta = -0.50128$. The parameter Π_2 is 0.88363 at $T_{LL} = 230.35$ K. The homogeneous nucleation temperature θ_1 of the strong liquid 1 cannot become greater than zero after a first-order transition at T_{LL} . There is no strong-to-fragile transformation above $\Pi_1 = 0.8575$ and 227.8 K upon heating and no fragile-to-strong transformation above $\Pi_2 = 0.88363$ and $T_{LL} = 230.35$ K upon cooling. Water remains a strong liquid above θ_{LL} and $\Pi_2 = 0.88363$ ($0.31 < P < 0.55$ GPa) with its existing θ_2 despite the disappearance of θ_1 . The line $T_{LL}(P)$ has an upper limit set by $\Pi_1 = 0.49003$ ($P \approx 0.176$ GPa).

The C_p increase at zero pressure below T_m proves that the LLPT at T_{LL} is always present at lower pressures for $\Pi_1 = \Pi_2$ and disappears at the negative pressure $\Pi_1 = \Pi_2 = -0.49616$ when the latent heat vanishes. The value of ϵ_{ls} at θ_g is 0.49916 when pressure is not applied and cannot be negative under pressure. The lower limit represents the other end of the first-order transition line and confirms that the stability limit of phase 3 is $P \approx -0.149$

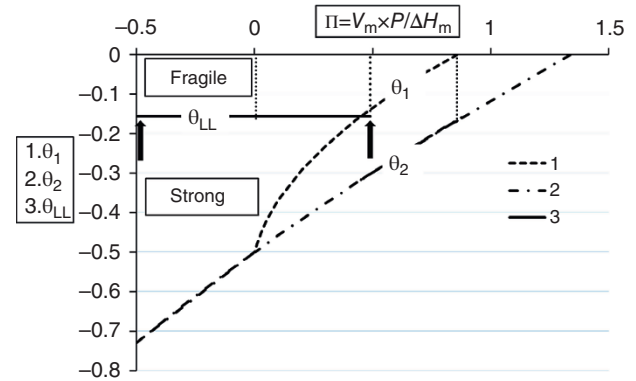


Figure 13 Phase diagram of supercooled water and strong liquids under pressure. Curves numbered from 1 to 3. 1, Reduced homogeneous nucleation temperature (θ_1) of strong liquid 1 vs. enthalpy coefficient Π induced by pressure P . 2, Reduced homogeneous nucleation temperature (θ_2) of strong liquid 2 vs. enthalpy coefficient Π induced by pressure P . 3, LLPT line separating the fragile liquid phase from the strong one at $\theta_{LL} = -0.15665$. Ends of the first-order transition line $T_{LL}(\Pi)$: $\Pi = -0.49616$, $P \approx -0.157$ GPa; $\Pi = 0.49003$, $P \approx 0.176$ GPa. Source: Reproduced with permission and adapted from [8], © Elsevier.

GPa assuming a density ρ of 0.9 g/cm³. This last critical point (Figure 13) is close to the maximum density evaluated at a negative pressure of 0.140 GPa [36], which contradicts previous conclusions [8] because pressure also acts on fragile liquid states. Above 0.31 GPa, the phase diagram is deeply modified by first-order transitions at $T_g = 0.65 T_m$.

In the P, T representation of the first-order transitions of supercooled water (Figure 14), the equilibrium line $P(T_{LL})$ is calculated with $T_{LL} = 0.84335 T_m$. The density is roughly estimated to be 0.9 g/cm³ for all negative pressures, and T_m obeys the Clausius–Clapeyron relation $dP/dT = -0.0134$ GPa/K. The transitions at T_{LL} and T_{sg} cannot take place at the same pressure: T_{LL} exists only for $-0.149 < P < 0.176$ GPa, and T_{sg} for $0.31 < P < 0.55$ GPa,

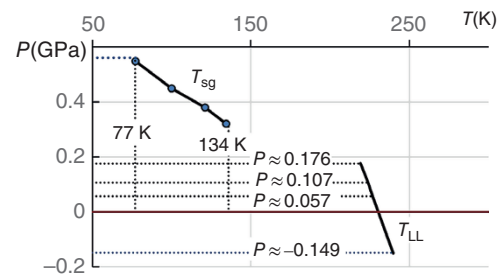


Figure 14 Diagram P, T of first-order transitions in supercooled water. T_{sg} : transformation temperatures LDA–HDA for $0.31 < P < 0.55$ GPa. T_{LL} : liquid–liquid phase transition for $-0.149 < P < 0.176$ GPa; for $P > 0.176$ GPa, disappearance of T_{LL} ; for $P = 0.057$ GPa and $P = 0.107$, the homogeneous nucleation temperatures are equal to T_m ; for $P < -0.149$, disappearance of strong phase 3.

Table 3 Dependence of the critical number n of supercluster atoms at T_g on melting entropy as calculated from Eq. (3).^a

Number	1	2	3	4	5	6
Materials	Pure metals	H ₂ O	GeO ₂	BeF ₂	SiO ₂	NaAlSi ₃ O ₈
ΔS_m (J/g.atom K)	9	7.33	4	19.3	1.49	3.65
n	83	102	187	390	505	211
θ_g	-0.6223	-0.5	-0.396	-0.285	-0.262	-0.2018
ϵ_{gs0}	0.217	0.6667	0.963	1.2462	1.3035	1.4538

^a $\epsilon_{gs0} = (3\theta_g + 2)/(1 - \theta_g^2)$ from Eq. (9) with $\Delta\epsilon = 0$ and experimental values of $\theta_g = (T_g - T_m)/T_m = \theta_{n-}$.

and T_{LL} is nonexistent for $P > 0.176$ when the enthalpy coefficients of fragile liquids at 230 K are greater than 2.

5 Supercluster Formation at the Glass Transition of Strong Liquids

Among strong and fragile liquids, d-mannitol [C₆H₁₄O₆] (Chapter 11), *n*-butanol [C₄H₁₀O], and triphenyl phosphite [P(OC₆H₅)₃] are receiving particular attention [24]. The enthalpy constraint for the formation of a glacial phase by isothermal annealing in these liquids is respected even though the relevant enthalpy difference then is $\Delta\epsilon_{lg}(\theta_{om}) - \Delta\epsilon_{lg0}$ instead of $\Delta\epsilon_{lg}(\theta_{om})$ only for LDA and HDA. A glass phase 3 having a frozen-in entropy close or equal to that of crystals can exist beyond the first glacial phase as observed for the second such phase of *n*-butanol [24]. For the three liquids, the glacial phase results from first-order transitions of fragile or strong liquids 2 without changing the enthalpy of liquid 1 [24]. A deep first-order transition from fragile to strong liquid 1 does not exist, contrary to that experienced by water at $T_{LL} \cong 227\text{--}230$ K, which could be related to its proximity to the triple point [13, 17, 18].

Turning now to SiO₂, we note a first similarity with H₂O in that the low-pressure phases of both substances are described as open networks of either OH₄ or SiO₄ tetrahedra. In SiO₂ phases, the marked contrast between strong Si—O intratetrahedral and weak Si—O—Si intertetrahedral bonds also results in a very rich polymorphism, with about 20 phases known [37], whereas two of these polymorphs, namely, quartz and cristobalite, exhibit a density minimum near 1300 K, the melting point of cristobalite in addition decreasing with pressure [38]. The OH₄ and SiO₄ units bonded in tetrahedral arrangements are spatially correlated, forming infinite clusters around T_m [11].

In SiO₂, the nucleation temperature in liquid 2 is T_g , like for H₂O and all other glasses. The critical number n of atoms in an elementary supercluster is predicted in Table 3 with Eq. (3) at $T_2 = T_g$ of any liquid 2. New ordered structures are built at T_g by superclusters whose

density decreases when the “magic” number n of atoms defining the critical size of elemental (probably icosahedral) superclusters is exceeded. The value of $(1 + \epsilon_{gs})/(\theta_g - \epsilon_{gs})$ in Eq. (3) is 1.5 in all glasses. This magic number n is $751/\Delta S_m$ with $\ln K = 90$ and $N_A k_B = 8.34$ J in Eq. (3) where ΔS_m is the melting entropy in J/K/g atom [39].

The atom number n per entity increases with the reduced glass transition temperature and facilitates percolation and interpenetration. For example, for H₂O, $n = 102$ and $\theta_g = -0.50128$ and for SiO₂, $n = 505$ and $\theta_g = -0.262$. The different bonding forces between H₂O and SiO₂ atoms and molecules induce different melting temperatures T_m and enthalpies ΔH_m , which are embodied in the definition of the reduced temperature θ . Despite this feature, the reduced glass transition temperature ($\theta_g = -0.50128$) of H₂O is smaller than that of SiO₂ (-0.262) because the weakness of Si—O intertetrahedral bonds, compared with those of O—H, makes the building of supercluster structure easier.

Being proportional to $[1 + \Delta\epsilon_{lg}(\theta_g)]^3/[\Delta\epsilon_{lg}(\theta_g)]^3$, the critical number of atoms giving rise to phase 3 diverges when $\Delta\epsilon_{lg}$ tends to zero at T_g [29]. The glass state in fact results from the percolation threshold of such entities at the homogeneous nucleation temperature $T_2 = T_g$ [40].

We finally note that vitrification is very difficult to achieve in the absence of atoms of different nature in pure metals (Chapter 7.10) at the lowest $\theta_g = -0.6223$ fixed by Lindemann’s constant of 0.103, corresponding to $\epsilon_{gs0} = 0.217$ [26]. In Figure 15, the homogeneous nucleation temperatures $T_2 = T_g$ of superclusters in some strong liquids 2 are plotted as a function of their enthalpy coefficients ϵ_{gs0} governing their formation between $\epsilon_{gs0} = 0.217$ and 2. The number of different atoms also increases the glass transition temperature.

6 Perspectives

As based on glass phenomenology and nucleation thermodynamics, a two-liquid model shows the existence of a univariant first-order transition curve $T_{LL}(P)$ between two critical pressures. To complement classical

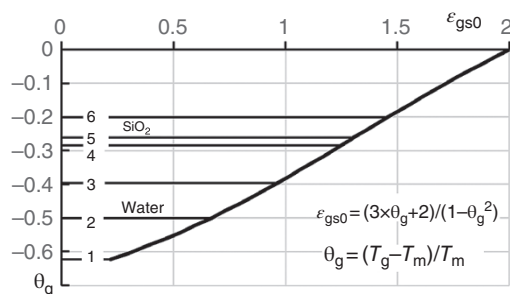


Figure 15 Reduced glass transition temperatures θ_g vs. ε_{gso} (cf. Table 3 for numbers 1–6). Formulae $\varepsilon_{gso} = (3\theta_g + 2)/(1 - \theta_g^2)$ and $\theta_g = (T_g - T_m)/T_m$ referring to Eq. (9) for $\Delta\varepsilon = 0$ and $\Pi_2 = 0$ with $\theta_{n-} = \theta_g$.

nucleation theory, an enthalpy term is introduced to account for the formation and the melting of glass nuclei through homogeneous nucleation of the liquid, instead of surface melting. The homogenous nucleation temperatures then show the thermodynamic origin of glass formation and the superheating temperatures of “ordered” liquids. Whereas these features begin to be revealed [24, references therein], overheated nuclei could even be viewed in a near future to unveil new properties of superatoms such as their melting by homogeneous nucleation instead of surface melting.

As a matter of fact, the first-order transition at T_{LL} under normal pressure induces the formation of a strong glacial phase as already observed in few materials [24]. A liquid-to-glass transition occurs for $0.017 < P < 0.55$ GPa. The existence of a pseudo-critical point calculated for $P = 0.018$ GPa is confirmed [12]. A line of first-order transitions at $P(T_{LL})$ exists for $0 < P < 0.55$ GPa in agreement with experimental results [7, 41]. Any negative pressure tends to induce crystallization near T_{LL} .

Like water, any melt could contain at least two liquid states, each one having its glass transition temperature at a homogeneous nucleation temperature T_1 or T_2 . The main glass transition would always occur at the temperature where the two ordered liquids are mixed, and a glass phase 3 was produced at $T_{g2} = T_g$.

The most interesting perspective for applications is the existence of first-order transition temperatures given by Eq. (17), leading to sharp transformations of glasses toward new equilibrium states of lower enthalpy, which may be the crystalline state, an ultrastable glass state, or a new equilibrium state of glass. These transformations can be produced by isothermal annealing each time that $\Delta\varepsilon_{lg}$, as given by Eq. (15), is equal or close to zero (cf. Figures 6, 11, and 12) with or without application of pressure. The lowest enthalpy of the ultrastable glass is obtained by vapor deposition at a well-defined temperature T_{sg} below T_g . Other first-order transitions giving rise to glacial

phases occur above T_g if $\Delta\varepsilon_{lg}$, as given by Eq. (15), is still close to zero, as exemplified by water (Figures 6, 11, and 12). These sharp transformations are difficult to achieve in bulk glasses or glass-forming melts because the exothermic enthalpies heat the sample and the condition $\Delta\varepsilon_{lg} = 0$ cannot be respected. To observe these sharp transformations, the supercooled liquid or the glass should be maintained close to the temperature of transformation. Despite this difficulty, such transformations of supercooled water have been produced in bulk samples [5–7].

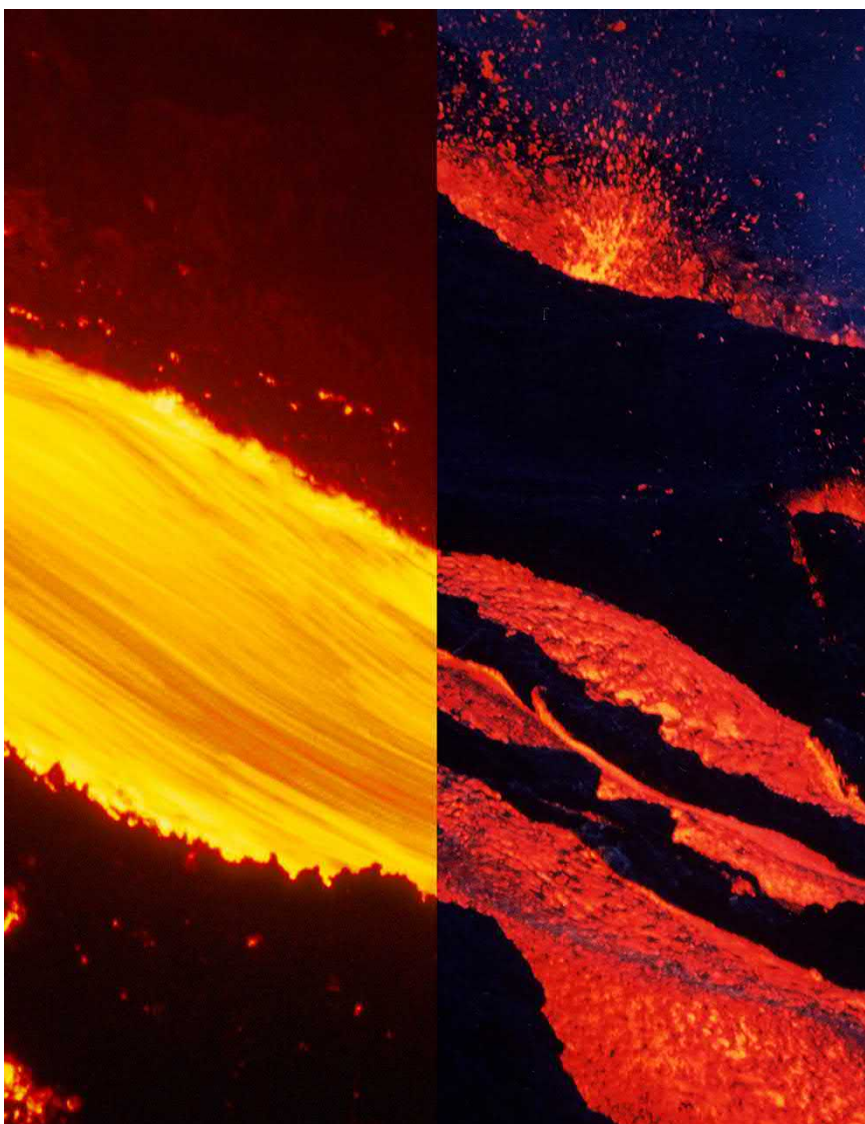
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Section IV. Transport Properties

Figure 1 A time immemorial illustration of the slowing-down effects of viscosity increases on mass transport: an initially yellow-hot, highly fluid basaltic lava (left) gushing down the slope of the Piton de la Fournaise volcano (La Réunion island) before cooling to a red-hot, slowly advancing, and partially crystallized magma (right). *Source:* Photos Nicolas Villeneuve.



This section is the shortest of the *Encyclopedia*, but certainly not the least important. It could have been part of the third since transport properties and their mechanisms are of course matters for physicists. But these properties deserve a special treatment owing to the fundamental kinetic control they exert on all processes involving glass-forming melts, whether industrial or natural. In industry, throughput is, for example, optimized through compromises made between faster processes and higher operating costs caused by higher temperatures and the ensuing wear of equipment. But the kinetics of all processes is ultimately limited by mass and heat transfer within the glass, which depends much on both temperature and composition as will be seen in this section.

That glass can be blown just by the pressure of human breath simply results from the Newtonian nature of the viscosity of oxide glasses, i.e. the strict proportionality between the strain rate and the stress applied. Empirically, it has long been known that viscosity is the single most important practical property of glass-forming liquids: from melting to shaping and annealing, all the operations of the glassmaker must be performed in well-defined intervals (Chapter 10.5). In nature (Figure 1), viscosity is also the key parameter that has determined the rate of mass and energy transport at all scales ever since the Earth and terrestrial planets formed 4.57 billion years ago. But an important practical difficulty underlined by J. Deubener is that no other property of glass-forming melts varies so much with temperature, at constant composition, and with composition, at constant temperature: in both cases variations can exceed 13 orders of magnitude, independently of the fact that solid and gaseous inclusions can also exert a strong influence (Chapter 4.1).

Even though viscosity is a bulk property, it is controlled in oxide melts by the mobility of network-forming cations, which vanishes at the glass transition. In contrast, the mobility of network-modifying cations can remain significant, which is why glasses can be poor electrical insulators. As described by J.-L. Souquet, ionic transport is generally ensured by the most mobile ions, i.e. the small and weakly bonded alkalis, whose motion conforms to the models of ionic transport designed for crystals, although an electronic contribution to electrical conductivity also exists in the presence of coexisting states of multivalent elements such as Fe^{2+} and Fe^{3+} between which electron transfer can occur (Chapter 4.2).

With decreasing temperatures, the increased decoupling between the mobilities of network formers and modifiers has important consequences on tracer diffusion coefficients, which also vary considerably with both composition and temperature. A considerable body of diffusion data is now available and even includes high-pressure measurements relevant to the earth sciences. It is reviewed by H. Ni and N. de Koker who emphasize the general decrease of diffusion coefficients with increasing charge, ionic radius, and polymerization state of the melt; they also point out that, in spite of the insights gained from atomistic simulations, work remains to be done to understand fully the microscopic mechanisms at play (Chapter 4.3). Contrary to the simple case of tracer diffusion, whereby a single element is considered, in many practical situations diffusion takes place between two melts of different compositions. On both sides of the diffusion front, one must consider the strong coupling between the motions of the diffusing elements that is determined by their mutual chemical affinities. The question is dealt with by M. Roskosz and E. Gouillart who explain how material fluxes in opposite directions can be coupled with Onsager generalization of Fick's equations; as an illustration, they apply this formalism to the determination of the diffusion matrices and diffusion pathways in ternary systems, from which more complicated situations can be treated (Chapter 4.4).

Heat transport must also be considered in terms of either thermal conductivity (k) or diffusivity (D), the latter differing from the former by the product of density and heat capacity. Determination of these properties is difficult at high temperatures where radiative transfer dominates. The ground has become firmer thanks to new methods examined by A. Hofmeister and A. Whittington with which decreases of both k and D with increasing polymerization have been documented; but more complex effects are seen with increasing temperatures as a result of the interplay of rising heat capacities and structural disorder in the liquid state, which in contrast hampers heat conduction (Chapter 4.5).

Among transport phenomena, diffusion lends itself the most readily to numerical simulations thanks to the possibility of tracking individual atomic pathways. As described by J. Habasaki, the complexity of the processes is clearly revealed by dynamic heterogeneities characterized by fractal dimensions and non-Gaussian dynamics as well as by a disruption of jump pathways at work in the mixed-alkali effect (Chapter 4.6).

4.1

Viscosity of Glass-Forming Melts

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1 Introduction

That Babylonians had already devised an empirical means to characterize viscosity (Chapter 10.11) was a very early recognition of the fundamental role played by this property in all glassmaking operations (Chapter 1.1). The great importance of not only viscosity but also of its temperature dependence has also been very long recognized, as indicated by the terms *short* and *long* used by glassmakers to indicate the time available for forming a cooling glass gob depending on the maximum length of the piece that could be stretched without being reheated. As a clear illustration of these statements, one should remark that in this *Encyclopedia* no other physical property is mentioned more frequently and in more chapters than viscosity. By itself, this central importance justifies the rather comprehensive account that will be given here from a dual experimental and theoretical standpoint.

By definition, viscosity designates the melt resistance to flow under shear or normal stresses. In this respect, glass-forming melts distinguish themselves from all other liquids by the fact that their viscosity may vary with temperature by 14 orders of magnitude or more. It is this feature that makes it possible to give glass almost any kind of geometry in an inexpensive way. Viscosity (η_0), for instance, determines the conditions for melting and refining (0.7–1.0, in log units of η_0 in Pa·s), melt flow in furnace parts (1.0–1.5), forming and afterworking (1.5–7.0), annealing and tempering (11–14) and it also specifies the upper temperature of use (>14) [1]. In nature, viscosity plays the same fundamental role in

determining the rate of magma ascent to the surface as well as the style of volcanic eruptions, from gently effusive to dramatically explosive (Chapter 7.2).

As long as a melt is homogeneous, its flow obeys Newton's law according to which the ratio between the stress applied and the resulting deformation rate is a constant at a given temperature. Owing to their importance, the conditions to be satisfied for Newtonian viscosity are presented in Section 2. Insights into the physical origin of the fluid behavior on atomic scales are then given in Section 3, where theoretical concepts of structural relaxation are introduced and linked to experimental data on the dynamics of their structural entities. The importance to control viscosity in glass manufacturing over a wide range of more than 14 orders of magnitude requires different measuring methods, which are presented in Section 4. Engineering aspects are also a leading motivation to find an accurate description of the temperature dependence of viscosity. Recent results illuminating the subject are shown in Section 5.

The dependence on composition, which arises from the change in the type and fraction of network formers, modifiers, and intermediates, is of practical importance for industry too. These compositional trends are visualized by *isokom* temperatures of equal viscosity in Section 6. Deviations from Newtonian viscosity are observed when the time to establish a steady-state flow exceeds the timescale of liquid deformation. Under these conditions, relaxation phenomena cause time-dependent viscosity and lead to shear thinning with respect to high deformation rates. Both effects are introduced in Section 7. Finally, Section 8 will shed light on the flow of heterogeneous liquids. In particular, suspension rheology is used to describe the effective viscosity of bubble- and crystal-bearing liquids as they appear in the course of either batch melting or magmatic processes.

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2 General Aspects and Definitions

Glass melts are characterized by a time-dependent response to either mechanical strain or stress. At temperatures above the glass transition T_g , they can be considered as incompressible isotropic fluids when steady-state flow obtains. Under these conditions, the flow conforms to Newton's law:

$$\tau_\sigma = \eta_0 \frac{dU}{dy}, \quad (1)$$

where the Newtonian viscosity η_0 is a constant of proportionality between the shear stress τ_σ and the derivative of the velocity component in the direction of the shear dU/dy , which is perpendicular to the displacement. In fact, only an apparent viscosity can be determined since U is measured in most experimental techniques from the change in position (angle ϕ , length l) in the direction of displacement. For a linear velocity gradient, dU/dy reduces to U/y , and the apparent viscosity η is equal to Newtonian viscosity η_0 . It is then given by the constant ratio between the applied shear stress τ_σ and the shear rate $\dot{\gamma}$ in the direction of displacement:

$$\eta_0 = \frac{1}{f} \frac{\tau_\sigma}{\dot{\gamma}}, \quad (2)$$

where f is a geometric coefficient that reflects the ratio of extensional (normal) to shear stresses (Trouton's ratio). A value $f=1$ applies for pure shear deformation (e.g. Couette and Searle-type rotational viscometers; see Figure 1), whereas $f=3$ is valid for the uniaxial elongation of a glass fiber (volume conservative flow of Poisson's ratio $\nu = 0.5$). For the latter, $\dot{\gamma}$ is replaced by the strain rate $\dot{\epsilon}$ (where $\dot{\epsilon} = d\epsilon/dt = [dl/dt]/l$, with l = fiber length) and the shear stress τ_σ by the normal stress σ , whereas for the former $\dot{\gamma}$ corresponds to the angular velocity $d\phi/dt$.

The SI viscosity unit is the Pascal second (Pa·s), where $1 \text{ Pa}\cdot\text{s} = 1 \text{ N}\cdot\text{s}/\text{m}^2 = 1 \text{ kg}/\text{s}\cdot\text{m}$. In industry, however, viscosity is still commonly expressed in terms of the CGS system whose unit is the poise (P). The conversion factor is $1 \text{ P} = 1 \text{ dPa}\cdot\text{s}$ (decipascal second) and vice versa $1 \text{ Pa}\cdot\text{s} = 10 \text{ P}$.

Newton's constitutive equation of a liquid requires the flow to be laminar; otherwise inertia would cause turbulence and the flow would become complex. Laminar flow means that a constant friction arises in a fluid between neighboring particles that are moving at different velocities in parallel layers. This situation obtains when values lower than 1 are found for the Reynolds number, which defines the ratio of inertial to viscous forces as $Re = \rho VL/\eta$ (ρ = density, V = fluid velocity, L = characteristic linear dimension). If this condition is not met, more general

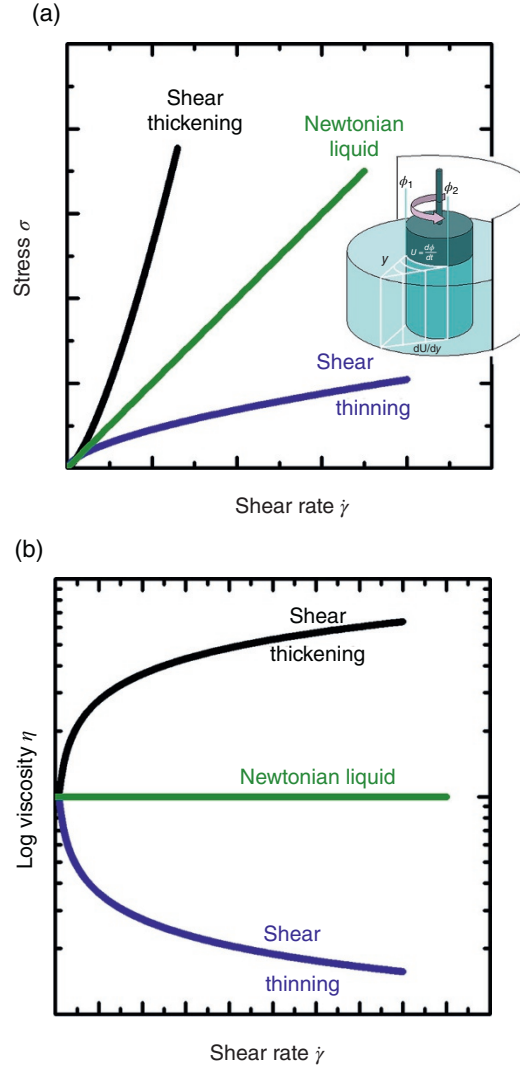


Figure 1 Flow of Newtonian and non-Newtonian liquids as characterized by stress (a) and viscosity (scaled logarithmically) (b) vs. strain rate. Inset: sketch of Newtonian laminar flow in a Searle-type rheometer with a stationary outer cylinder and a rotating inner cylinder (no-slip condition). Gradient in the angular velocity dU/dy perpendicular to the direction of the shear forces and the angular velocity $d\phi/dt$.

non-Newtonian formalisms must be used. If the stress is very quickly applied or if the liquid is heterogeneous (e.g. suspension, foam, emulsion), the complex flow of glass-forming melts can, for instance, be described with power law equations [2]:

$$\tau_\sigma = \tau_{\sigma 0} + K \dot{\gamma}^n, \quad (3)$$

where $\tau_{\sigma 0}$ is the yield stress, K the flow consistency and n the exponent of the strain rate. In contrast to Newtonian fluids ($\tau_{\sigma 0} = 0$), plastic materials begin to flow only when the applied stress exceeds this minimum value $\tau_{\sigma 0}$. If the

non-Newtonian liquid has no yield stress, then the apparent viscosity η is a function of its current deformation rate:

$$\eta = \frac{1}{f} \frac{\tau}{\dot{\gamma}} = K \dot{\gamma}^{n-1}. \quad (4)$$

For $n = 1$, Eq. (4) reduces to Newton's law, whereas for $n < 1$ and > 1 the liquid is shear thinning ($\eta < \eta_0$) and shear thickening ($\eta > \eta_0$), respectively. These differences between Newtonian and non-Newtonian liquids are summarized in Figure 1.

3 Structural Aspects

Above the glass transition, structural relaxation is much faster than usual times of observation so that Newtonian liquids do not retain any memory of their flow history. Understanding the physical origin of viscous flow in glass-forming melts requires insights onto the dynamics of their structure, however, which is by definition controlled by the structural relaxation time τ (Chapter 3.7). At the atomic scale, theories generally assume that energy is required to overcome potential energy wells delineated by the bonds connecting the structural elements that undergo flow. The flow causes irreversible dissipation of mechanical energy (internal friction) since as soon as it is stopped the liquid returns to its initial mechanical state.

With respect to viscous flow, the relevant structural elements are atoms, molecules, or network fragments (polyhedra). They are nonperiodically distributed in space and linked to one another, creating a potential energy landscape where minima are separated by barriers having varying heights and shapes (Chapter 3.9). These elements are thermally agitated, performing small motions around their equilibrium positions. In metastable melts at low enough temperatures (i.e. close to the glass transition), a sufficiently large stress is necessary to overcome the relevant potential energy wells, whereas in stable melts at very high temperatures (i.e. far above the liquidus), thermal agitation is significant and induces fast displacements over distances that can reach the size of an element (with trajectories resembling those of a Brownian movement). Under these conditions, relaxation times are relatively short ($\tau < 10^{-12}$ seconds), and one would expect a smooth increase of the viscosity with decreasing temperature since the mean thermal velocity of an atom decreases with $T^{0.5}$. As stated in Section 5, however, the actual dependence of viscosity on temperature is orders of magnitude steeper.

As a matter of fact, the slowing down of the relaxation dynamics correlates with a considerable broadening in the time dependence of the correlation function. A two-step decrease is evident. At short timescales, atoms can move by fast dynamics in a collision regime (Brownian atoms); at intermediate timescales, they remain thermally agitated but become trapped locally (large displacements being prevented), leading to a plateau in the correlation function; at relative large timescales, they can escape from their neighborhood by means of faster β -relaxation and slower α -relaxation, whereas the correlation function decays in a stretched exponential form (Kohlrausch–William–Watts type) [3]. The stretching exponent indicates the dynamically heterogeneous nature of the relaxation in glass-forming melts, which can be interpreted in two different ways: (i) either of different atoms showing different dynamical timescales in a spatially homogeneous melt (ii) or of a spatially heterogeneous melt in which all atoms of a given local environment relax at the same timescale, these timescales differing from one environment to another. The multi-atom problem of dynamic heterogeneity is echoed in terms of cooperative rearranging regions by Adam and Gibbs [4].

As for the temperature dependence of viscosity, it means that fast-collision dynamics are prevalent far above the liquidus, whereas α -relaxation is predominant close to the glass transition. In sodium silicate melts, ^{23}Na spin–lattice relaxation NMR experiments [5] indicates that the dynamics of Na hopping follows the timescale for stress relaxation by viscous flow at temperatures above T_1 ($\eta = 10^1$ Pa·s). At lower temperatures the timescale of β -relaxation processes meets that of viscous flow, whereas the crossover temperature for the β -to- α transition is close to T_3 for a common soda-lime-silicate melt (see Section 5). For temperatures below T_3 , viscous flow is controlled by the timescale of α -relaxation, which controls the dynamics of the bridging O–Si bond connecting two silica tetrahedra [6]. Below the glass transition, isostructural viscosity is finally observed since the timescale of α -relaxation and then exceeds that of the experiment.

Emphasizing the importance of the bridging oxygen dynamics, Bockris et al. [7] identified network fragments such as $\text{Si}_3\text{O}_9^{6-}$ rings as basic “flow units” in metastable alkali silicate melts, whereas Toplis et al. [8] assigned subsystems of approximately 10 “activated” tetrahedra at the glass transition as an effective dynamic length scale. In any case, a decrease in the dynamic length scale with temperature can be assumed because experiments show that the Stokes–Einstein and Eyring equations (both relating self-diffusion coefficient to viscosity) break down at

Table 1 Standard (fixed) points for fast determination of the viscosity–temperature relationship of technical glasses, with $\eta_0(T_n) = 10^n$ Pa·s.

Point	n	Standard procedure, Ref.	Method
Working	3.0	ISO 7884-5	Sinking bar
Half-sphere	3.25	[9]	Heating microscopy (m)
Half-sphere	3.55	[9]	Heating microscopy (p)
Sphere	5.1	[9]	Heating microscopy (p, m)
Softening	6.6	ISO 7884-6, JIS 3103-1, ASTM C338	Fiber elongation (m)
Deformation	7.2	[9]	Heating microscopy (m)
Sintering onset	9.0	[9]	Heating microscopy (p)
Annealing	12.0	JIS 3103-1, ASTM C336	Fiber elongation (m)
Annealing	12.2	ISO 7884-7	Beam bending(m)
Glass transition	12.3	ISO 7884-8	Dilatometric expansion (m)
Strain	13.5	JIS 3103-1, ASTM C336	Fiber elongation (m)
Strain	13.7	ISO 7784-7	Beam bending (m)

Keys: p = powder compact, m = monolithic specimen.

temperatures below $\approx 1.2 T_g$, where viscous flow is decoupled from the length scales of diffusion.

4 Technological Aspects

4.1 Measuring Methods

It should not come as a surprise that a physical property that varies by 14 orders of magnitude cannot be measured with a single experimental method. Two different kinds of rheometers or viscometers are actually used depending on the predominantly liquid- or solid-like response of the material when subjected to a stress (Tables 1 and 2) [9]. The first operates in viscosity ranges relevant to the melting, fining, and working processes ($\eta_0 < 10^6$ Pa·s) and involve melt shearing under controlled conditions of either strain rate (rotating concentric cylinders) or stress (rising bubbles and falling spheres). The second kind is applicable to highly viscous melts ($\eta_0 > 10^6$ Pa·s) in ranges at which deformation and annealing are performed industrially (Figure 2). Viscosity is then frequently determined by the rate at which a glass specimen of defined geometry deforms under a constant load (with a combination of shear and volume stresses), as made with ball-penetration, beam-bending, and cylinder-compression experiments (Table 2).

Application of these methods relies on the assumptions that the flow is laminar and that η depends neither on time or deformation rate, i.e. that Eq. (2) is valid ($\eta = \eta_0$). The former has to be considered if glasses are deformed close to the glass transition ($\eta_0 = 10^{11}$ – 10^{15} Pa·s), where relaxation times are large (see Section 7)

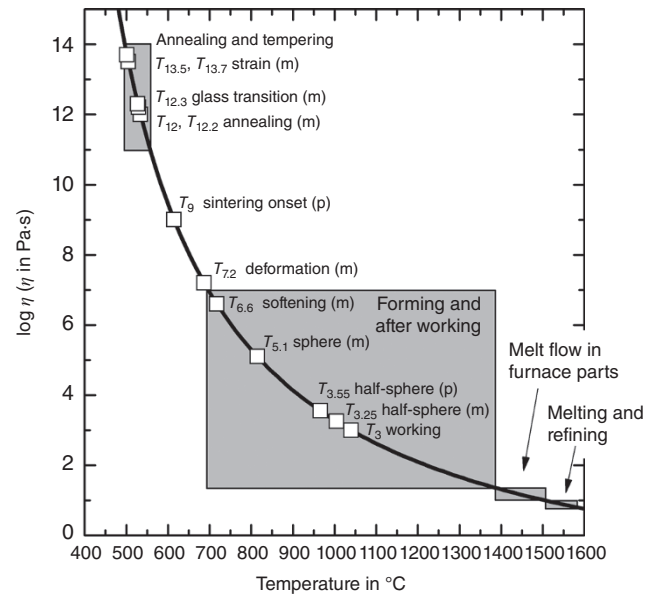


Figure 2 Viscosity–temperature range of industrial processes (boxes) and fixed points of viscosity T_n (with $\eta_0(T_n) = 10^n$ Pa·s) for a soda-lime-silica glass.

so that increasingly long measuring times t become necessary to achieve complete relaxation. In practice, for isothermal treatments, these holds should be $t > 10^{2.5}$ seconds at T_{11} with $\eta_0(T_{11}) = 10^{11}$ Pa·s, $t > 10^{3.5}$ seconds at T_{12} , $t > 10^{4.5}$ seconds at T_{13} , etc., which means that under standard laboratory conditions, very high viscosities ($\eta_0 > 10^{15}$ Pa·s) seem unattainable. Accordingly, when a glass specimen is heated at a constant rate such as at 5 K/min, equilibrium values of the viscosity are derived from Eqs. (8) to (12) if $\eta < 10^{9.5}$ Pa·s.

Owing to the very strong temperature dependence of viscosity, accurate measurements require temperature gradients within the sample investigated to be less than about 0.1 and 1 K near the glass transition and above the liquidus, respectively. Finally, phase transitions such as partial evaporation or crystallization are generally incongruent processes, whose resulting composition changes cause marked viscosity variations. A simple way to make sure that they are not problematic during long, high-temperature measurements thus is to check that the same viscosities are obtained at given temperatures at the beginning and end of the experiments.

4.2 Gas Bubble Rise

This method is specially relevant to glass refining because it relies on measurements of the terminal ascent velocity $(dh/dt)_0$ of a gas bubble in a translucent crucible (silica, corundum) as recorded by a camera system through the observation window of a high-temperature furnace. Under low Reynolds numbers (<1), the ascent of small gas bubbles ($2r < 2\text{--}3\text{ mm}$) obeys Hadamard–Rybczynski's law, Eq. (5) in Table 2, whereas that of larger ones deviates from it because of bubble deformation (oblate ellipsoidal and spherical cap).

4.3 Falling Sphere

If an observation furnace is not available, a small noble metal sphere (Pt, Pt/Rh) may be dropped in the hot melt where it falls for a time t . The penetration depth h of the sphere until the melt is quenched is measured on longitudinally cut quenched samples or continuously by *in situ* X-ray scans. Under low Reynolds numbers (<1), the terminal velocity $(dh/dt)_0$ obeys Stokes' law (Reynolds number-to-drag coefficient ratio is 24), but edge effects have to be accounted for if capsules and narrow crucibles are used (Table 2). The method is time consuming because an experiment yields the viscosity at a single temperature. Hence, it is now mainly used for high-pressure determinations for which no other methods are applicable.

4.4 Rotating Cylinder

The method is the most common for fluid melts ($\eta < 10^3\text{ Pa}\cdot\text{s}$). The torque M needed to maintain a constant rotational speed $(d\phi/dt)_0$ is measured for either a rotating spindle immersed in the hot melt of a fixed container (Searle type) or a rotating crucible in which a fixed spindle is immersed (Couette type). A correction to account for the drag of the container walls is in principle necessary (Eq. 7 of Table 2), but in practice one determines

deviations from ideal geometric conditions by running initially the system with liquids (reference oils) of certified viscosity at room temperature. Measurements are thus relative and not absolute.

4.5 Fiber Elongation

Near the glass transition, viscosity can be determined from the rate of elongation of a fiber either under its own weight (one face fixed) or under an external load. In the former, the fiber is only partially heated over its length (see fixed points of viscosity; Section 4.10), whereas in the latter the entire fiber is placed inside a furnace. A fiber of length l with rounded tips is then clamped between two supports and elongated in a vertical or horizontal furnace at a constant force. If a weight is used, the deformation stresses increase because of contraction of the fiber diameter. A spiral disk that maintains a constant stress level compensates this effect. For small fiber (mass $m < 4\text{ g}$) in a vertical stage, the elongation rate dl/dt has to be corrected for self-loaded elongation and surface tension-induced shrinkage. The viscosity for a full-length heated fiber of mass $> 4\text{ g}$ is given by Eq. (8).

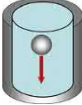
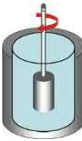
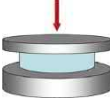
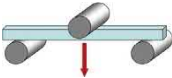
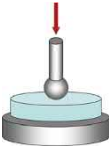
4.6 Parallel Plate

In this method, the deformation of a cylindrical disk uniaxially compressed is measured in a vertical tube furnace after a hold time for thermal equilibration. Rigid pistons or push rods exert controlled strain rate or load conditions. Depending on the slip conditions between the glass faces and the contact material, barreling of specimen may be observed. For perfect non-slip conditions and a sample with an initial diameter-to-height ratio ≥ 1 , the Gent solution is given by Eq. (9) where h is the instantaneous height and dh/dt is the axial deformation rate. Owing to the high exponential dependence of the viscosity on the height in Eq. (9), deviations from ideal stiffness of the apparatus during compression must be considered.

4.7 Beam Bending

The resistance to bending of a beam is yet another measure of viscosity. The symmetric three-point bending method is the most common. A glass beam of support span l is centrally loaded inside a furnace after a hold time for thermal equilibration. Hagy's solution of the measured deflection rate dh/dt at midpoint for a rectangular beam of cross-sectional height h and width b (moment of inertia $I_c = h^3b/12$) is given by Eq. (10).

Table 2 Methods of measuring viscosity.

Method	Schema	Range ($\log \eta$)	η (Pa·s) =	Equation
Gas bubble rise		<2	$\frac{r^2 g \rho_{\text{melt}}}{3(dh/dt)_0}$ ^a	(5)
Falling sphere		<4	$\frac{2r^2 g (\rho_{\text{sphere}} - \rho_{\text{melt}}) C_1}{9(dh/dt)_0}$ ^b	(6)
Rotating cylinder		1–5	$\frac{MC_2}{(d\varphi/dt)_0}$ ^c	(7)
Fiber elongation		>6	$\frac{mgl}{3\pi r^2 (dl/dt)}$	(8)
Parallel plate		>7	$\frac{2\pi mgh^5}{3V(2\pi h^3 + V)(dh/dt)}$	(9)
Beam bending		>7	$\frac{gl^3 (m + hbl\rho_{\text{glass}}/1.6)}{144I_c (dh/dt)}$	(10)
Sphere penetration		>8	$\frac{3mg}{16(2rh)^{0.5} (dh/dt)}$	(11)
Rod torsion		>11	$\frac{2lM}{\pi r^4 (d\varphi/dt)}$	(12)

Keys: r = radius (m), ρ = density (kg/m^3), g = gravitational acceleration (m/s^2), V = volume (m^3), l = length (m), h = height (m), b = width (m), m = mass (kg), M = moment of force (torque) ($\text{N}\cdot\text{m}$), I_c = moment of inertia (see text) C_1 and C_2 .

^a Solution of Hadamard–Rybczynski's equation for a fluid sphere and a Reynolds number-to-drag coefficient ratio of 16, which allows for slip velocities at the bubble surface.

^b Faxen correction term $C_1 = 1/[1 + 2.4 (r_{\text{sphere}}/r_{\text{container}})]$ for $r_{\text{sphere}}/r_{\text{container}} < 0$, to which must be added a correction for the penetration depth $h_{\text{melt}} = h_{\text{glass}}[\rho_{\text{melt}}/\rho_{\text{glass}}]^{1/3}$ to account for the difference in the specific volumes of the melt and the glass.

^c Correction for the drag of the container walls given by a Faxen-type term. For a rotating spindle of length l (Searle type), it is

$$C_2 = \left(r_{\text{container}}^2 - r_{\text{spindle}}^2 \right) / \left[8\pi l r_{\text{spindle}}^2 r_{\text{container}}^2 \right].$$

4.8 Sphere Penetration

In this method, a rigid high-precision microsphere of radius r (e.g. sapphire with $r < 1\text{--}2\text{ mm}$) is fixed between the lower end of a transducer rod and the surface of the glass specimen in a vertical furnace setup. The rod is loaded after a hold time for thermal equilibration and the sphere starts to penetrate at a rate dh/dt , where h is the penetration depth into the glass. The viscosity is then given by the solution of Douglas et al. for $r \gg h$ of Eq. (11).

4.9 Rod Torsion

A rod of length l and radius r is fixed at one end and the opposite end is rotated with a torque M to maintain the angular velocity $d\phi/dt$. In cross sections along the heated length l of the rod, the angular velocity decreases from $d\phi/dt$ at the rotating part to zero at the fixed part. The viscosity is given by Trouton and Andrews' solution to Eq. (12) for a rod subjected to torsion in either horizontal (limited by bending at higher temperatures) or vertical (limited by flowing at lower viscosities) positions.

4.10 Standard (Fixed) Points

In industry, determination of viscosity over the entire temperature range relevant to production (from the batch melting to the cooling regime) is time consuming. In practice, therefore, glass technologists frequently make only a few measurements (at least 3) to compute the entire viscosity–temperature curve with any of the three-parameter equation presented in Section 5. Following standard procedures, they rely on standard points, also referred to as viscometric fixed points. A standard point is by definition an isokom temperature. Depending on the geographic region (market), slightly different standards are selected today in industry as seen in Table 1 with ISO, JIS, and ASTM.

Because the use of fixed points still requires three individual measurements, Scholze [10] proposed a single heating microscopy experiment on a small glass volume (monolith or powder compact) as an even faster method to determine the entire viscosity–temperature relationship. The method relies on the small temperature coefficient of the surface energy of silicate liquids. The onset of shrinkage (glass powder compacts), the rounding of edges (bulk glass cubes/cylinders), and the appearance of sphere and half-sphere shaped geometries of the sessile drop then take place within narrow viscosity intervals independent of the composition of technical glasses (soda-lime-silicate and borosilicate). All these characteristic geometries (silhouettes) can thus be observed in a microscopy experiment as the glass specimen is heated at a constant rate on an alumina support.

Besides, other fixed points such as the flow (T_2) and the melting (T_1) temperatures are used in industry to characterize the fusibility of silicates (slags, enamels, ashes) following in-house and product-specific procedures. In most of them the volume of the glass specimen is defined, which will not enable an exact determination of viscosity since differences in density and surface tension of glasses are not taken into account. For soda-lime-silica melts, the viscosity values ($n = \log \eta_0$) of the isokom temperatures used in industry are compiled in Table 1.

5 Temperature Dependence of Viscosity

5.1 Viscosity Regimes

Viscosity varies so much with temperature that its ratio between the liquidus T_{liq} and glass transition temperatures T_g is about 10^6 (silica glass), 10^{11} (soda-lime-silicate), and 10^{15} (metal alloys). When a broad temperature range is considered (Figure 3), the Newtonian flow of glass-forming liquids can be divided into three parts [11].

Below the glass transition (stage I of Figure 3), the average time required for structural relaxations τ exceeds the observation time t , and the viscosity follows an Arrhenian law. A constant activation energy indicates that relaxation involves only vibrational contributions, configurational

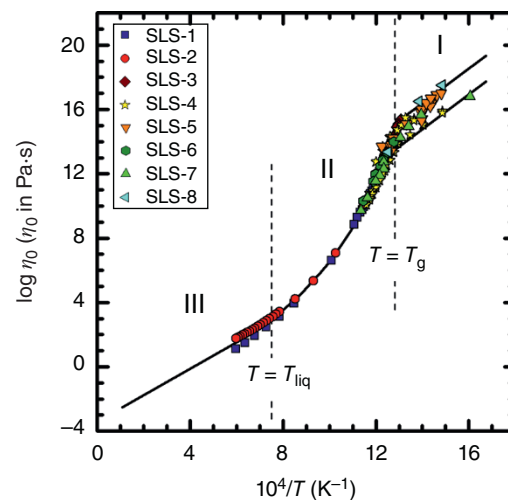


Figure 3 The three viscosity regimes of soda-lime-silica melts of similar composition (window glass). Stage I ($T < T_g$): isostructural Arrhenian viscosity of the non-relaxed liquid, the upper and lower lines referring to the two limiting fictive temperatures. Stage II ($T_{\text{liq}} > T > T_g$): non-Arrhenian viscosity, with a VFT fit through the data. Stage III ($T > T_{\text{liq}}$): Arrhenian viscosity, with a linear fit through the data with $\eta_{\infty} = 10^{-3.5}\text{ Pa}\cdot\text{s}$. Crossover temperature assumed to be close to T_{liq} ($\approx 1015\text{ K}$).

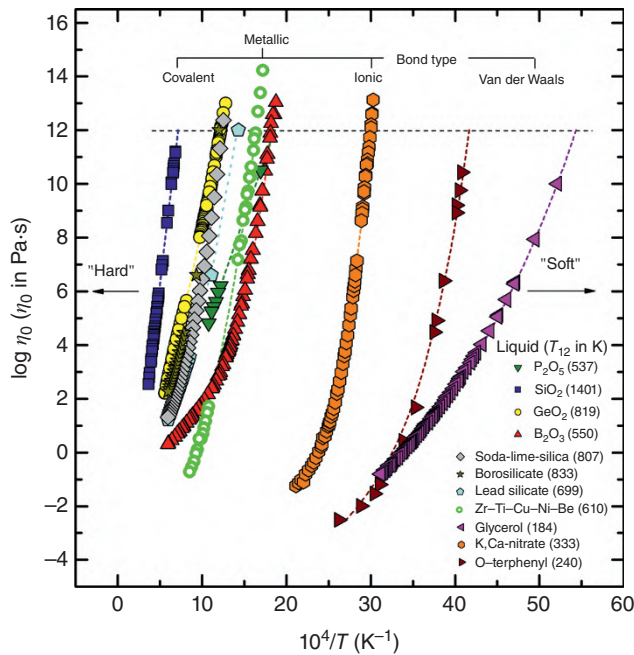


Figure 4 The *hard* and *soft* character of a variety of glass-forming liquids as determined by the nature of bonding: Arrhenius plot of the viscosity of the main network-forming oxides P_2O_5 , SiO_2 , GeO_2 , and B_2O_3 (bases of the phosphate, silicate, germanate, and borate glass families, respectively), of technical silicate melts (soda-lime-silica, borosilicate, and lead silicate), and of glass-forming metallic (Zr–Ti–Cu–Ni–Be alloy), van der Waals (glycerol, *o*-terphenyl), and ionic (K,Ca-nitrate) liquids. Dashed lines: VFTH fits through the data to approximate T_{12} for those liquids for which viscosity data are not provided.

changes being left unexplored. The viscosity of such an unrelaxed liquid is called isostructural. It is measured in a rheometric experiment instantaneously after a sudden temperature change. In this way the activation energy at constant structure may be obtained – *constant structure*, meaning here constant configurational entropy, free volume, packing density, or any other parameter embodied in a particular model. In the glass transition range (GTR), the observation and relaxation times become similar so that one can monitor changes

in viscosity toward its equilibrium value during long enough experiments.

Between T_g and T_{liq} (stage II of Figure 3), the observation time t is in general longer than τ . For most glass-forming liquids, the viscosity becomes non-Arrhenian (Figure 4). In the Arrhenius expression (Eq. (13)), a temperature dependence of the activation energy $\Delta E = \Delta E(T)$ is thus required:

$$\eta_0 = \eta_\infty \exp\left(\frac{\Delta E(T)}{kT}\right), \quad (13)$$

where η_∞ is the viscosity at infinite temperature and k is the Boltzmann constant. From T_g to T_{liq} , viscous flow is governed by configurational contributions to cooperative rearrangements, which involve all atoms of the rearranging regions. Besides the change in concavity of the viscosity–temperature curves (Figure 4), one observes a shift to higher temperatures with increasing bond strength, ranging from weak van der Waals to strongly covalent bonds. On this basis, glass technologists distinguish *soft* from *hard* glasses, which have high and low isokom temperatures, respectively.

Above the liquidus (stage III of Figure 3), the variation of viscosity with temperature in the third region is Arrhenian again since configurational contributions are less dominant and the rearrangement is governed by the local atomic excitations, which goes in line with a more disassociated state of glass-forming liquids at high temperatures. The atomic vibration period τ between successive assaults to pass the energy barrier is on the order of 10^{-14} seconds as $T^{-1} \rightarrow 0$. Maxwell's equation then yields $\eta_\infty = 10^{-3.5}$ Pa·s for glass-forming silicate melts with a shear modulus at infinite frequency G_∞ of about 30 GPa.

5.2 Viscosity–Temperature Relationships

Equations with three constants have been developed to account for changes with temperature in the size of the activated volume, i.e. for the deviation from an Arrhenian temperature dependence of the viscosity (Table 3).

Table 3 Frequently used three-parameter (A , B , C) equations to represent the temperature dependence of viscosity between T_g and T_{liq} .

Name (acronym)	Year	$\log \eta_0 =$	Equation	Ref.
Vogel–Fulcher–Tammann–Hesse (VFTH)	1921–1926	$A_1 + \frac{B_1}{T - C_1}$	(14)	[12]
Adam–Gibbs (AG)	1965	$A_2 + \frac{B_2}{T \ln(T/C_2)}$	(15)	[4]
Avramov–Milchev (AM)	1988	$A_3 + \left(\frac{B_3}{T}\right)^{C_3}$	(16)	[17]
Mauro–Yue–Ellison–Gupta–Allan (MYEGA)	2009	$A_4 + \frac{B_4}{T} \exp\left(\frac{C_4}{T}\right)$	(17)	[18]

Among these the empirically Vogel–Fulcher–Tammann–Hesse (VFTH) equation (14) is most frequently used [12]. This equation relates $\Delta E(T)$ to $1/(T - C_1)$, an assumption that leads to a viscosity divergence as $T \rightarrow C_1$. Different theoretical models have been proposed as the basis of the VFTH equation. They rely on the assumption that activation energy depends either on free volume [14–16] or on configuration entropy $S^{\text{conf}}(T)$, i.e. $\Delta E(T) \propto S^{\text{conf}}(T)^{-1}$ [4].

Since both vibrational and configurational entropy may contribute to entropy changes, different approaches have been proposed to extract the configurational part in the Adam and Gibbs (AG) model. The solution for $S^{\text{conf}}(T)$ is, for instance, given by Eq. (15) for the assumptions that the isobaric heat capacity ΔC_p is temperature independent and that a glass below T_g and the corresponding liquid above T_g have the same vibrational entropy, that is, $S^{\text{conf}}(T) = S(T) - S^{\text{vib}}(T)$. In contrast to the AG approach, the Avramov–Milchev (AM) equation (16) is based on an atomic hopping model, i.e. viscosity is assumed to depend on the total entropy $S(T)$, not on configuration entropy only [17]. This model assumes a constant jump frequency (10^{14} seconds $^{-1}$) for activated transitions and a temperature-dependent Poisson distribution for the local potential energy barrier opposing viscous flow. This leads to a stretched exponential dependence of viscosity with temperature, where the stretching exponent C_3 represents the kinetic fragility (see Section 5.2) of the melt. Mauro, Yue, Ellison, Gupta, and Allan based their viscosity equation (17) on the Adam–Gibbs model but related the configurational entropy to the topological degrees of freedom each atom can access [18].

In 1984 Richet [19] showed that the verification of $S^{\text{conf}}(T)$ of the AG model can be carried out by an additional calorimetric experiment. In his approach $S^{\text{conf}}(T)$ is determined from the sum of its value at the glass transition $S^{\text{conf}}(T_g)$ plus the additional configurational entropy produced with increasing temperature from T_g to T . The former term is the effective residual entropy (by assuming ergodicity of the system at $T \leq T_g$, i.e. $S^{\text{conf}}(T_g) = S_{\text{glass}}(0)$), whereas the latter term is found by the integration of the configurational heat capacity $\Delta C_p^{\text{conf}} = a + bT$, which is the heat capacity increment at T_g ($\Delta C_p^{\text{conf}} = C_{p\text{liquid}}(T) - C_{p\text{glass}}(T_g)$) such that $S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + a(\ln[T/T_g]) + b(T - T_g)$. Richet's solution for $S^{\text{conf}}(T)$ is given by Eq. (18) where the constants a , b of the linear heat capacity function and T_g are to be derived from calorimetric experiment through the GTR [19]:

$$\log \eta = A_6 + \frac{B_6}{T \left(S_{T_g}^{\text{conf}} + a \ln(T/T_g) + b(T - T_g) \right)} \quad (18)$$

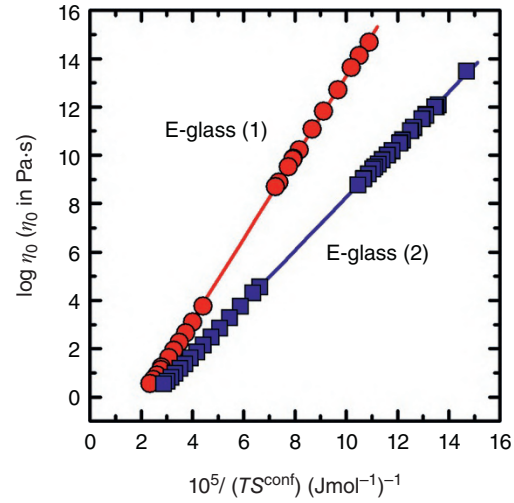


Figure 5 Adam–Gibbs (AG) linear representation of the temperature dependence of the viscosity of two calcium borosilicate (E-glass) melts (Chapter 1.5).

If additionally $S^{\text{conf}}(T_g)$ is known from calorimetry for the glass under consideration, then Eq. (18) reduces to a two-parameter (A_6 , B_6) equation, i.e. a plot of $\log \eta$ vs. $(TS^{\text{conf}})^{-1}$ requires only linear fitting through the data (Figure 5).

5.3 Scaling with Temperature and Master Diagrams

In general, the ratio of the activation energy of stage II to III is ≥ 1 as illustrated by the change in slope in the Arrhenius diagram (Figure 4). The concavity of the viscosity–temperature curve depends on the nature of the glass-forming liquid, which ranges between the two limiting groups of 3-D connected networks of covalent bonded tetrahedra (small change in slope) and molecular/ionic liquids and liquids with hydrogen bonds (large change in slope). Within this classification an increase in the curvature is observed with decreasing bonding dimensionality and decreasing bond strength, which represents the transition from *long* to *short* glasses.

Viscosity in the GTR was analyzed by Nemilov [20] ($\Delta E(T_g)$) and Laughlin and Uhlmann [21] (scaling to T_g/T) to distinguish between these groups. In 1985 Angell [22] introduced the names *strong* and *fragile* glass formers to reflect the stability of their short- and medium-range order against temperature-induced structural degradation. The strong–fragile pattern with a range of kinetic fragilities $m = [d(\log \eta)/d(T_g/T)]_{T_g}$ varying from ≈ 17 (SiO_2) up to 200 (van der Waals liquids) is represented in T_g -scaled Arrhenius plots of the liquid viscosities (Figure 6). For this purpose, $\eta(T_g)$ must be defined with respect to the heating rate and measurement frequency.

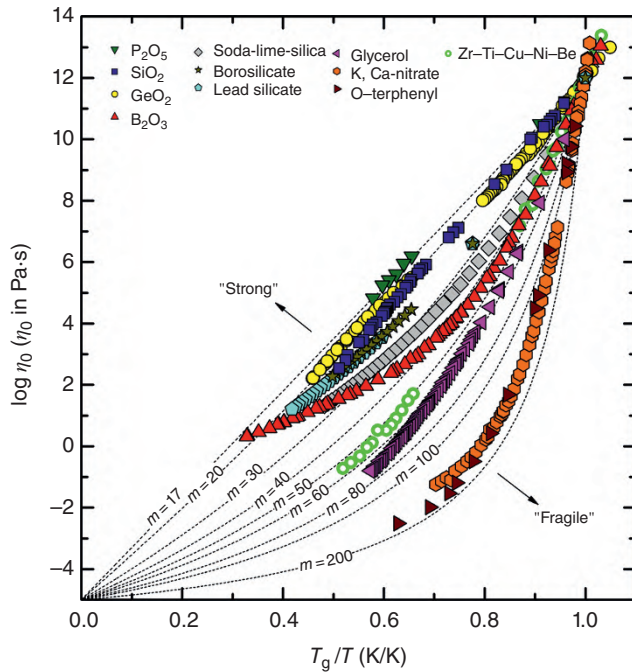


Figure 6 From strong to fragile liquids: fragility (m) and T_g/T -scaled representations of the temperature dependence of the viscosity of a variety of glass-forming melts (T_g defined as T_{12}). Viscosity and T_{12} data from Figure 4. Isofragility lines shown for $\eta_0(T_g) = 10^{12}$ Pa·s and $\eta_\infty = 10^{-5}$ Pa·s indicated by arrows.

If the average relaxation time τ (T_g) = 10^2 seconds is used, then the viscosity (in log units) at T_g is 10.5 for molecular liquids and 12.5 for silica glass. With $T_g = T_{12}$, i.e. $\eta(T_g) = 10^{12}$ Pa·s, Eqs. (19)–(21) can be rewritten to fit viscosity data to the reduced temperature scale (T_g/T) directly from the parameters η_∞ , m , and T_g (Table 4). Alternatively, the liquid fragility can be expressed by the parameters $C_3 = m/(12 - \log \eta_\infty)$ [23], $F = C_1/T_g$ [24], and $F_{1/2} = 2T_g/T_{1/2} - 1$ with $\log \eta_0(T_{1/2}) = (12 - \log \eta_\infty)/2$ [25].

Further, one can represent the departure from Arrhenius laws by plotting the viscosity (in log units) against $dT/d(\log \eta_0)$. This type of scaling is frequently used to approximate limits with respect to specific working processes such as drawing, blowing, and casting as the

isokomal workability is proportional to the change in temperature per viscosity decade. Thus, this type of temperature scaling visualizes best the technologist's classification of *long* [large $dT/d(\log \eta_0)$] and *short* [small $dT/d(\log \eta_0)$] glasses (Figure 7).

A master diagram has been developed, which collapses the different $\eta(T)$ dependences of Figure 6 onto a single curve over the stage II viscosity interval [26] through incorporation of the crossover temperature T_c (which indicates the α -to- β transition in governing the rheology) as a second reference temperature into the temperature scaling. The resulting master curve is represented by the dimensionless plot $\log[\eta(T)/\eta(T_g)]$ vs. $[T_c/(T_c - T_g)] \times (T_g - T)/T$ of Figure 8 where T_c is determined from relaxation studies or, if not provided by an independent experiment, estimated from fits of the viscosity to the general dependence of Figure 8.

6 Composition Dependence

6.1 Pure Oxide and Binary Silicate Melts

Oxide glasses are the focus of this section owing to their technological importance. In general the viscosity depends much more on composition and structure near the glass transition (T_{12}) than above the liquidus ($<T_3$) where data tend to converge. Isokom temperatures are used to visualize the changes in viscosity with composition.

The isokoms of glass-forming melts do not correlate simply with the activation energy of viscous flow ΔE or other interatomic energies, e.g. SiO_2 (1450; 525), BeF_2 (590; 250), and Se (300; 1670) with T_{12} in K, ΔE in kJ/mol [20]. A prediction based on metal–oxygen bond strength and the dimensionality of the polyhedral linkage also fails for pure oxide melts with a spatially continuous network for which T_{12} (Figure 4) is 1401 K (SiO_2), 819 K (GeO_2), 550 K (B_2O_3), and 537 K (P_2O_5). In addition, the isokom temperatures of these oxides are strongly affected by impurities. Traces of other elements are mainly introduced by the raw materials and contamination during the

Table 4 Equations representing the temperature dependence of viscosity in terms of reduced temperatures (T_g/T), kinetic fragility m , and $\eta(T_g) = 10^{12}$ Pa·s.

Acronym	$\log \eta_0 =$	Equation
VFTH	$\log \eta_\infty + \frac{(12 - \log \eta_\infty)^2}{m(T/T_g - 1) + (12 - \log \eta_\infty)}$	(19)
AM	$\log \eta_\infty + (12 - \log \eta_\infty)(T_g/T)^{m/(12 - \log \eta_\infty)}$	(20)
MYEGA	$\log \eta_\infty + (12 - \log \eta_\infty) \frac{T_g}{T} \exp \left[\left(\frac{m}{12 - \log \eta_\infty} - 1 \right) \left(\frac{T_g}{T} - 1 \right) \right]$	(21)

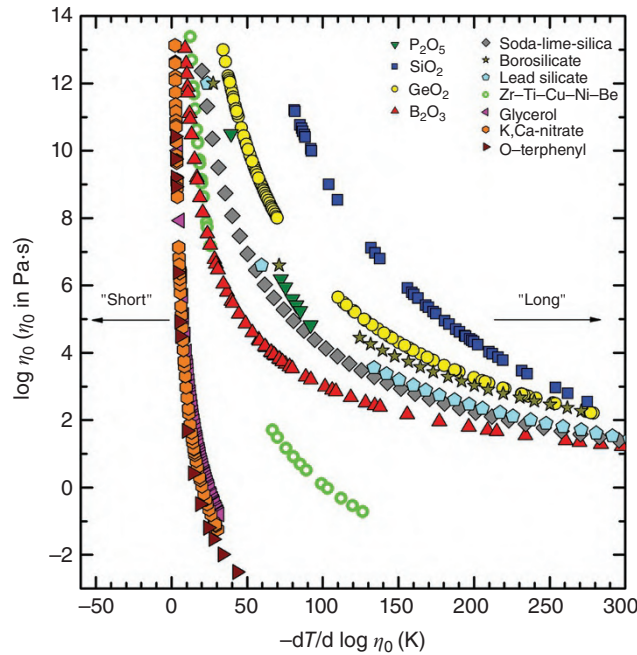


Figure 7 From *short* to *long* glasses: the poor or good isokomal workability of glass-forming melts seen in the $dT/d(\log \eta_0)$ -scaled representation of viscosity.

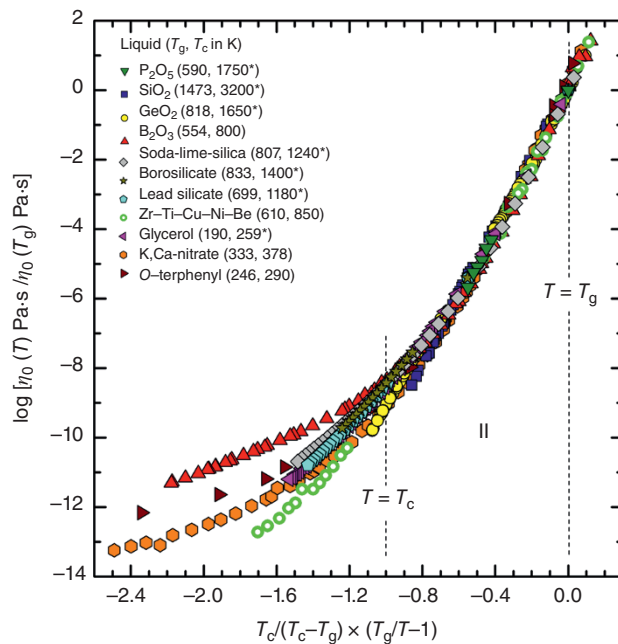


Figure 8 Master curve for the Stage II viscosity regime ($T_{liq} > T > T_g$) in plots of $\log[\eta(T)/\eta(T_g)]$ vs. $[T_c/(T_c - T_g)] \times (T_g - T)/T$ [28].

fusion process. As classified by Brückner [27, 28] for silica glass (types I–VII), the nature and fraction of impurity atoms play a crucial role in decreasing viscosity. Leko et al. [29], for instance, showed that small fractions of

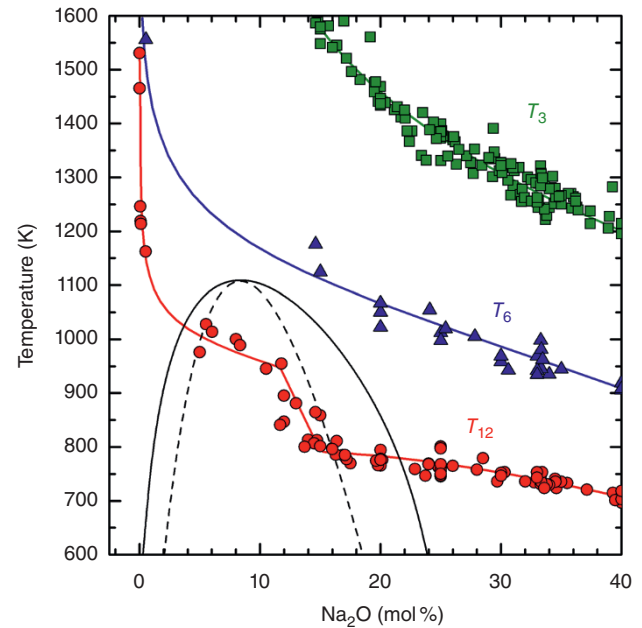


Figure 9 The markedly differing effects of additions of Na_2O to SiO_2 on the T_{12} , T_6 , and T_3 isokoms. Immiscibility dome (solid curve) and spinodal (dashed curve) included. Trend lines as guides to the eyes.

sodium atoms in silica melts lead to a dramatic decrease in the T_{12} isokom whereas the effect is less pronounced at higher temperatures (Figure 9). The main structural feature affecting viscosity is the formation of nonbridging oxygens (NBO), which depolymerize the tetrahedral network (Chapter 2.4).

When increasing the concentration of network-modifying ions from the impurity level to constitutional fractions (binary silicate melts), one has to take into account microstructural effects caused by the presence of stable and metastable immiscibility regions on the silica-rich part of binary $\text{M}^{2+}_{2/z}\text{O}-\text{SiO}_2$ ($\text{M} = \text{Li}^+, \text{Na}^+, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$) systems. The steep decrease in the T_{12} isokom is close to the spinodal boundary (12–16 mol % Na_2O) at which the silica-rich phase ceases to be continuous (Figure 9). The influence of divalent cations such as CaO , MgO , and ZnO at low temperatures departs from that of the alkalis. A steeper viscosity–temperature curve is observed because the T_{12} isokom increases with CaO and ZnO contents whereas the opposite effect holds for the T_3 isokom. These oxides are thus said by technologists to *shorten* the glass. The influence of MgO is similar to CaO , but at high temperatures (T_3) NBO formation becomes partly ineffective because of a reduction of the oxygen coordination from six to four. The addition of heavy post-transition metal cations such as Pb^{2+} to silica causes an even stronger viscosity decrease than by alkaline earth cations of similar size (Sr^{2+}) since their higher electron polarizability makes shear easier.

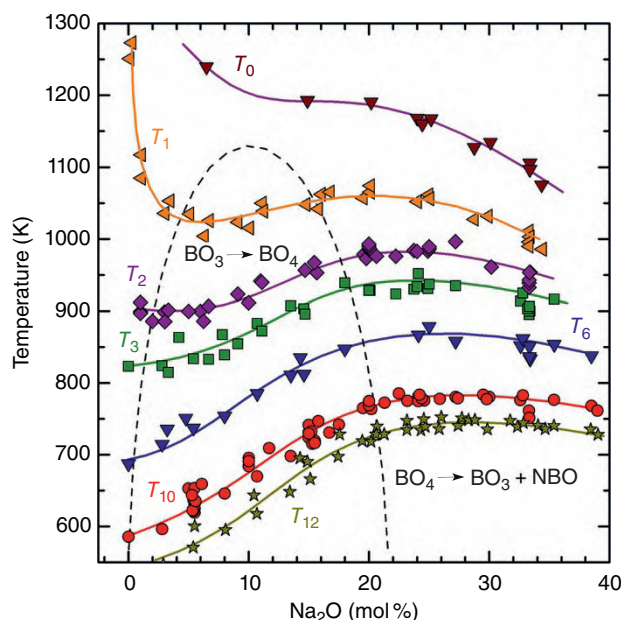


Figure 10 Effects of Na_2O content and induced changes in boron speciation on high- and low-temperature isokoms of the B_2O_3 – Na_2O system. Viscosity increases caused by BO_3 –to- BO_4 conversion delineated by the dashed domain.

Network-modifying oxides act as fluxes when mixed with SiO_2 , GeO_2 , and P_2O_5 . When added to B_2O_3 , Na_2O in contrast increases isokom temperatures up to about 20 mol % Na_2O at low temperatures (Figure 10) because of the conversion of triangular BO_3 groups into BO_4 tetrahedra stabilized by Na^+ . This effect is known as the boron anomaly (Chapter 7.6). At both higher Na_2O fractions and temperatures, however, NBOs are increasingly formed in a competitive process, which leads to the expected decrease in viscosity.

In phosphate melts, the viscosity is also closely related to the structure, which is a chain-like linkage for the metaphosphate compositions of monovalent $[\text{MPO}_3]$, divalent $[\text{M}(\text{PO}_3)_2]$, and trivalent $[\text{M}(\text{PO}_3)_3]$ metal cations. Eisenberg et al. [30] have early shown that an increase of the T_{12} isokom is caused by the high attractive forces of the metal cation at the terminal oxygen (TO), i.e. by an increasing ratio of the charge-to-metal oxygen distance $z/R_{\text{M-O}}$ (Figure 11). A structural explanation is that each metal cation has at least four terminal oxygens (TO) at the same or neighboring phosphate chains [31] and that removal of at least one TO at a time from the coordination sphere of the metal cation enables internal rotation of phosphate chains and, thus shear, to take place.

6.2 Ternary and Multicomponent Silicate Melts

The melts commonly used in the float- and container-glass industry are close to the archetypal ternary composition 16 Na_2O ·10 CaO ·74 SiO_2 (wt %). But actual

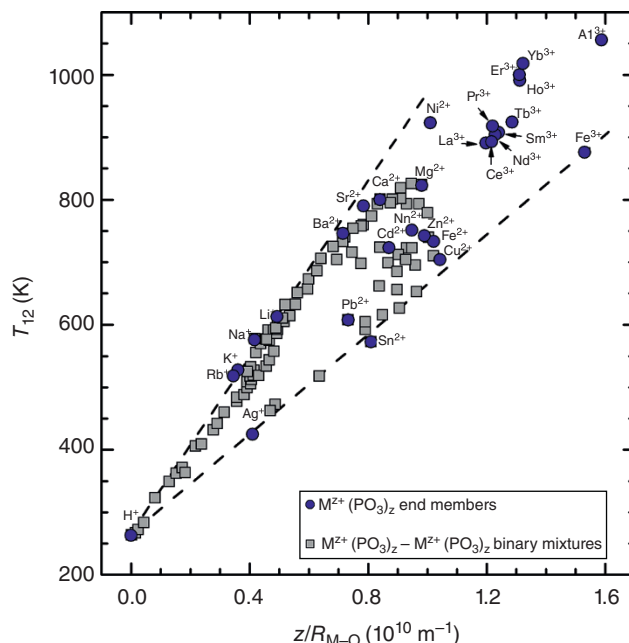


Figure 11 Influence of the charge-to-distance ratio $z/R_{\text{M-O}}$ on the viscosity of metaphosphate melts ($\text{O/P} = 3$) with mono- ($z = 1$), di- ($z = 2$), and trivalent ($z = 3$) metal cations M .

compositions include further former, modifier, and intermediate metal oxides and volatiles (sulfur, water) as exemplified by a typical float-glass composition of 71 SiO_2 , 0.5 Al_2O_3 , <0.1 Fe_2O_3 , 4 MgO , 10 CaO , 14 Na_2O , 0.1 K_2O , 0.3 SO_3 . Within limited compositional ranges, the effects on isokom temperatures of changes in oxide fractions can be described by linear functions (Chapter 1.1). The coefficients (oxide factors) for T_2 are positive for SiO_2 and Al_2O_3 , Fe_2O_3 and negative for MgO , CaO , Na_2O , and K_2O , whereas at low temperatures (T_{12}) the oxide factors for MgO and CaO are in contrast positive.

The viscosity of melts with two network-forming oxides has been studied systematically ever since borosilicate glass was introduced by Schott in the second half of the nineteenth century. Owing to the maximum in the fraction of BO_4 groups and the absence of NBO, the isokoms along the SiO_2 – $\text{Na}_2\text{O} \times 5.25\text{B}_2\text{O}_3$ tie line are important to the glass industry. At lower temperatures, however, an immiscibility region obtains with an upper critical temperature of about 1033 K so that isokoms can no longer be defined in view of the biphasic character of the Na_2O – B_2O_3 – SiO_2 metastable liquids [32].

Another system with two network former oxides relevant not only to industry but also to geochemistry is $\text{M}^{z+}_2/\text{zO}$ – Al_2O_3 – SiO_2 where Al^{3+} can replace Si^{4+} in tetrahedral sites if charge-compensated by alkali or alkaline earth cations (Chapter 2.4). For the molar ratio $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{M}^{z+}_2/\text{zO}) = 1$ of the meta-aluminous composition, a

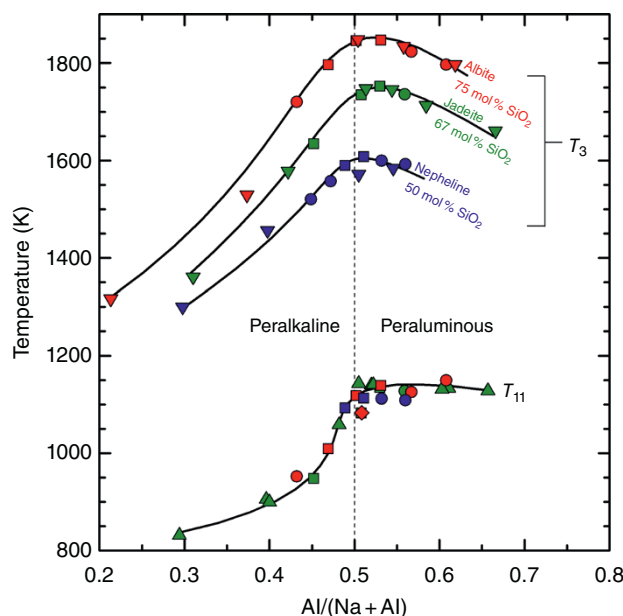


Figure 12 Influence of the $\text{Al}/(\text{Na} + \text{Al})$ ratio and associated change in aluminum speciation on the T_{11} and T_3 isokoms of sodium aluminosilicate melts of constant SiO_2 content (75, 67 and 50 mol %). The trend lines as guide to the eyes. Maximum shifting with increasing temperature to the peraluminous region.

fully polymerized network is expected with a maximum isokom temperature for melts of constant SiO_2 fraction. A maximum is actually observed for sodium aluminosilicate melts at high temperatures (T_3), but it is located slightly at the peraluminous side, whereas only a plateau is visible at low temperatures for the T_{11} isokom (Figure 12). Depending on the type of charge-compensating metal cation, the shift is caused by the presence of fivefold coordinated Al species [33] and (Si,Al) triclusters [34], which are involved in the flow mechanism of peraluminous melts near the meta-aluminous join. Likewise, structural investigations in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system at high temperatures indicate that the NBO fraction per tetrahedron (NBO/T) is minimum but not zero for the meta-aluminous composition [35].

6.3 Effects of Water

Water is a strong fluxing agent. Its solubility varies slightly with temperature but strongly with composition and especially with pressure since it increases initially approximately as the square root of the water pressure. As a result, solubilities higher than 10 wt % (or than 25 mol %, on an oxide basis) are observed at pressures on the order of 500 MPa (5 kbar). But determining the effects of large water contents of viscosity has long been hampered by the difficulty of high-pressure measurements.

The situation thus changed when it was recognized that high-pressure experiments could be restricted to the synthesis of hydrous samples whose viscosities could then be measured at room pressure down to $10^{9.5}$ Pa·s, before the kinetics of exsolution becomes significant, and could even be extrapolated to high temperatures by appropriate means [36].

Along with previous data for low water contents, the wealth of data obtained in this way has been interpreted in terms of the coexistence of structurally bonded OH groups and molecular $\text{H}_2\text{O}(\text{m})$ in the silicate network [37]. The solubility of these species depends on composition and is strongly nonlinear for a total water content below ≈ 2 wt % but linear above this value [38]. As for the OH/ $\text{H}_2\text{O}(\text{m})$ ratio, it positively correlates with temperature [39]. In practice, this ratio is about 10^3 for a technical (soda-lime) silicate melt under ambient water pressure (total water < 0.1 wt %), whereas it can reach 0.2 for geo-compositions for total water content of about 10 wt %.

If water speciation in metastable hydrous melt relaxes to the equilibrium value down to the glass transition, a three-component model can be used to reveal the individual contributions of OH groups, $\text{H}_2\text{O}(\text{m})$, and the “dry” network on T_g [40]. Expanding the database with viscosities of hydrous silicate melts and normalizing the T_{12} isokom to its value of the dry melt (set as 0.02 wt % total water), one finds that the data collapse on a master curve whose equation is [41]

$$\frac{T_{12}^{\text{hydrous}}}{T_{12}^{\text{dry}}} = \frac{1.01w_G + 0.22(Aw_{\text{OH}} + Bw_{\text{H}_2\text{O}(\text{m})})}{w_G + w_{\text{OH}} + w_{\text{H}_2\text{O}(\text{m})}}, \quad (22)$$

where $A = 30$, $B = 5$ and w_G , w_{OH} , and $w_{\text{H}_2\text{O}(\text{m})}$ are the weight fractions of the dry glass and water as OH groups and H_2O molecules, respectively (Figure 13).

6.4 Empirical Predictions from Composition

Predictions of viscosity as a function of temperature and glass composition are essential for industry. Present models are based on large data sources such as those provided by SciGlass and Interglad. They employ matrix algebra, nonlinear regressions, and structured chemical models, support multicomponent queries, and yield fast data presentations and viscosity predictions based on various property models.¹ The range of applicability of these models includes almost all known types of oxide glasses with a core competence in silicates. Other models have

¹ For instance, SciGlass (<http://www.akosgmbh.de/sciglass/sciglass.htm>) and Interglad (http://www.newglass.jp/interglad_n/gaiyo/info_j.html).

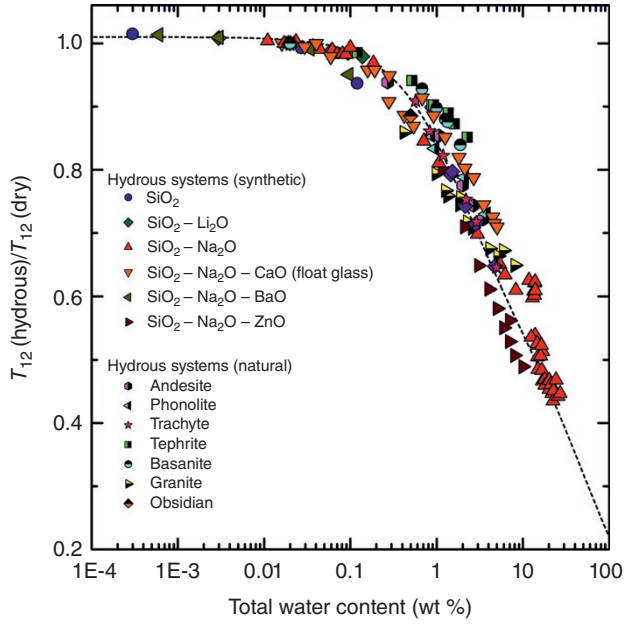


Figure 13 Strongly depressing effects of water content on the viscosity of hydrous melts as represented by the $T_{12}(\text{hydrous})/T_{12}(\text{dry})$ ratio for synthetic and natural silicate melts. Dashed curve: predictions of Eq. (22) with $A = 30$ and $B = 5$.

been proposed [42–44]. Isokom curves can be generated with the help of glass data information systems.

7 Dependence on Time and Strain Rate

7.1 Time-Dependent Viscosity

After a sudden temperature change, a time-dependent viscosity is commonly observed in the GTR. In these experiments a glass specimen is first equilibrated at a temperature T_{f1} and then suddenly brought to the new temperature T_{f2} at which the viscosity is measured. Depending on whether $T_{f2} < T_{f1}$ or $T_{f2} > T_{f1}$, the viscosity increases or decreases with time toward the equilibrium value $\eta_0(T_{f2})$, respectively (Figure 14), in a time much longer than that needed to establish the new temperature and to relax stresses by viscous flow (see Section 7.3). Transient effects of viscosity are governed by the relaxation of the liquid toward its equilibrium structure at T_{f2} . The viscosity–time curve for $T_{f2} < T_{f1}$ and $T_{f2} > T_{f1}$ follows generally a stretched exponential dependence:

$$\frac{\eta(t) - \eta(t = \infty)}{\eta(t = 0) - \eta(t = \infty)} \bigg|_{T_{f2}} = 1 - \exp \left(- \frac{t}{\tau} \right)^n, \quad (23)$$

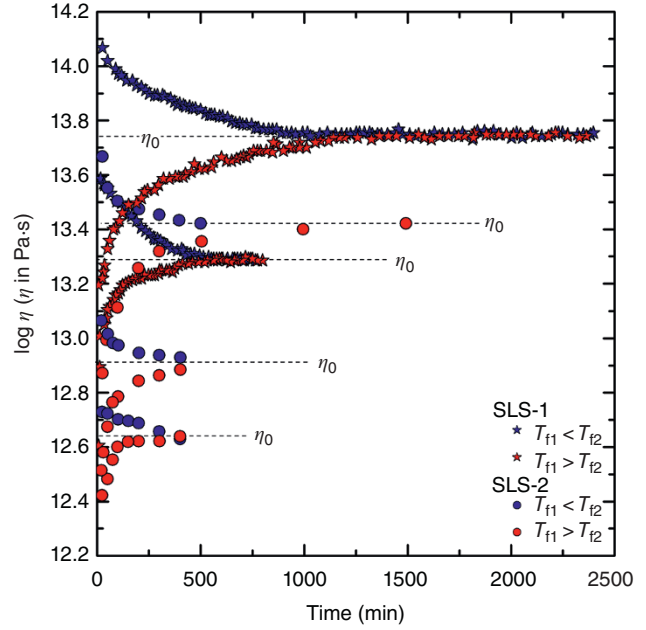


Figure 14 Increasingly slow viscosity relaxation with decreasing temperatures for soda-lime-silica glasses of different thermal histories after a sudden change in temperature from T_{f1} to T_{f2} .

where $\eta(t = 0)$ is the instantaneous (isostructural) viscosity, $\eta(t = \infty)$ the equilibrium viscosity η_0 , τ the structural relaxation time, and n the stretching exponent ($n < 1$).

7.2 Strain Rate-Dependent Viscosity

Another complication is the strain rate-dependent viscosity measured when the relaxation time for viscous flow approaches the inverse strain rate $1/\dot{\epsilon} = dt/d\epsilon$ of the deformation experiment. Under these extreme conditions, an apparent shear thinning is observed in experiments with deformation modes such as fiber elongation and cylinder compression. If the strain rate is normalized with the Maxwell stress relaxation time $\tau_\sigma = \eta_0/G_\infty$, the onset of the non-Newtonian flow is found at values three orders of magnitude lower, i.e. $\dot{\epsilon}\eta_0/G_\infty = 0.001$ (Figure 15). The flow curves and the apparent viscosity are influenced strongly by the dissipation of mechanical energy in the form of heat. Viscous heating and the temperature-induced decrease in viscosity have to be considered on the basis of an energy balance between heating and radiation effects, which depends mainly on the surface-to-volume ratio (A/V) of the deformed glass samples. For fibers, the change in temperature is negligible ($\Delta T \approx 0$), but for other geometries, viscous heating can exceed the heat loss at the surfaces ($\Delta T > 0$) and has therefore to be taken into account to make a clear distinction

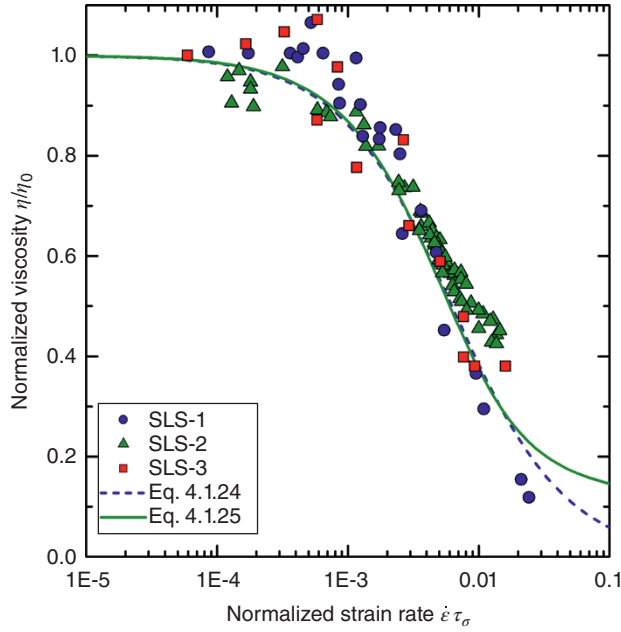


Figure 15 Dependence of the normalized apparent viscosity η_{app}/η_0 on the normalized strain rate $\dot{\epsilon}\tau_\sigma$ for homogeneous soda-lime-silica glasses.

between the structural and thermal effects causing shear thinning.

Simmons et al. [45] showed that shear thinning can be described by a simple relationship between reduced viscosity and the normalized strain rate function $\dot{\epsilon}\tau_\sigma/\alpha$:

$$\frac{\eta_{app}}{\eta_0} = \frac{1}{1 + (\dot{\epsilon}\tau_\sigma/\alpha)}, \quad (24)$$

where $\eta_{app} = \sigma/\dot{\epsilon}$ is the apparent non-Newtonian viscosity and the factor α is the ratio between the maximum stress sustained by the liquid and the instantaneous shear modulus of the glass (σ_{limit}/G_∞). This equation is valid for stationary states when stress increases caused by increasing strain rates are counterbalanced by stress decreases induced by dissipative heat fluxes ($\Delta T \approx 0$). Under these conditions, the limiting viscosity η_∞ is assumed to approach zero as $\dot{\epsilon} \rightarrow \infty$. Yue and Brückner [46] have characterized in terms of the flow relaxation rate $\dot{\epsilon}_g$ the transition from the relaxed state of the Newtonian fluid to the unrelaxed flow of the highly stressed fluid. The latter is represented by the onset of a pseudo-Bingham flow in which the apparent viscosity is lower than in the Newtonian regime, but no longer strain rate dependent, i.e. $\eta_\infty > 0$. In this way, Yue and Brückner derived Eq. [46]:

$$\frac{\eta_{app}}{\eta_0} = \frac{\eta_\infty}{\eta_0} + \frac{\dot{\epsilon}_g}{\dot{\epsilon}} \left(1 - \frac{\eta_\infty}{\eta_0}\right) \left(1 - \exp\left(-\frac{\dot{\epsilon}}{\dot{\epsilon}_g}\right)\right). \quad (25)$$

Non-Newtonian flow in glass-forming liquids is assumed to originate in viscoelastic relaxation processes related to orientation-produced stresses. The observation of flow and frozen-in birefringence of fibers during drawing and after quenching, respectively, has been used to quantify the degree of structural orientation (strained network fragments) involved in shear thinning.

7.3 Non-Newtonian Flow and the Glass Transition Range

The transition from the relaxed state of the Newtonian fluid to the final brittle fracture via the unrelaxed non-Newtonian flow under high stress levels is closely related to the definition of the GTR. Assuming a Maxwell stress relaxation, one can replace the observation time t , which is not relevant to the glass transition induced by an external control parameter, i.e. the strain rate $t = 1/\dot{\epsilon}$, to define the GTR in terms of Reiner's rheologic Deborah number (De) as [47]:

$$GTR = De = \frac{\dot{\epsilon}\eta_0}{G_\infty} = 1. \quad (26)$$

Scaling of GTR with Eq. (26) reveals that the time needed to establish the equilibrium viscosity after a sudden temperature change is related to $De = 10^{-2}$, whereas the onset of shear thinning takes place at $De = 10^{-3}$ (Figure 16). Both results indicate that stress relaxation is too fast to cause transient effects and strain rate-dependent viscosity. But they emphasize that the characteristic times involved in structural relaxation, which are related to long-range cooperative rearrangements of the equilibrium structure, are slower by a factor of up to 1000 than for relaxing stress through shorter structural pathways.

The melt fracture is closely related to $De = 1$ if one considers glass geometries of large A/V ratio, such as double-ring bended thin glass panes. The fracture of the melt is related to the limiting elastic response of the strained bonds under stresses exceeding a critical level. If viscous heating is involved, fracturing events can already occur at lower strain rates ($De = 10^{-1.5} - 10^{-2}$) through formation of temperature gradients and, therefore, of stress concentration in the less strained parts of the sample.

8 Dependence on Microstructure

8.1 Heterogeneous Melts

The presence of a microstructure leads to an increasingly complex viscous flow as a result of controlled phase formation (glass-ceramic and foam-glass products), of batch-to-melt reactions when granular raw materials

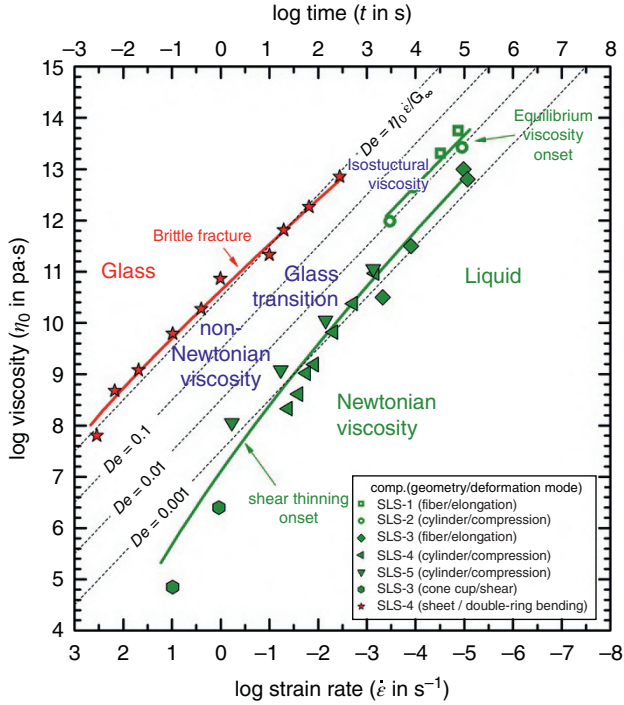


Figure 16 From brittle fracture to shear thinning: dependence of viscosity on time (strain rate) for homogeneous soda-lime-silica glasses. Solid lines: visual guides; dashed lines: liquid-to-solid transitions based on stress relaxation (Maxwell model with $G_{\infty} \approx 30$ GPa) and normalized to Reiner's Deborah number definition, Eq. (26). Newtonian flow expressed by the time- and strain rate-independent viscosity η_0 requiring structural relaxation of the liquid, i.e. two to three orders of magnitude longer times than Maxwell stress relaxation, $De = 10^{-2} - 10^{-3}$. For soda-lime-silica glass, $\eta_0(10^2 \text{ seconds}) = 10^{9.5} - 10^{10.5} \text{ Pa}\cdot\text{s}$.

react to form the bubbly unfined (“fresh”) melt, or of uncontrolled devitrification, liquid unmixing of degassing in industrial or geological contexts. Because of the metastability of supercooled liquids, the fractions of precipitated crystals and secondary liquids increase in general with time below the liquidus or critical temperature, respectively. A time-dependent rheology then is observed not only because of the physical effects resulting from the coexistence of two phases but also because the chemical composition of the residual melt changes continuously.

At temperatures close to the glass transition, the involved transformation kinetics are generally slow, which enables rheometric measurements to be made under quasi-stationary microstructural conditions, i.e. at constant fractions of secondary crystals, bubbles, and liquids, which are dispersed in the volume of the residual liquid matrix ([48, 49] and other early papers having relied on this assumption). Under these conditions, heterogeneous liquids can be treated as suspensions. One can then define the suspension-to-matrix ratio of the viscosity by

$$\eta_{\text{rel}} = \frac{\eta_{\text{susp}}}{\eta_0}, \quad (27)$$

where η_{rel} is the relative viscosity, η_{susp} the effective viscosity of the suspension, and η_0 the Newtonian viscosity of the liquid continuous matrix.

8.2 Crystal-Bearing Melts

The laminar flow of liquids is generally hindered by the presence of rigid inclusions, which cause an increase in the flow resistance of the suspension, i.e. $\eta_{\text{rel}} > 1$. The increase depends on the volume fraction of rigid crystals ϕ and their size distribution and shape. For dilute ($\phi < 0.03$) monodispersed suspensions of spheres, Einstein [50] derived the linear equation ($\eta_{\text{rel}} = 1 + B_E \phi$ with $B_E = 5/2$). The factor B_E is the intrinsic viscosity or Einstein coefficient for which the values proposed for different systems range from $3/2$ to $10/2$. For a non-dilute suspension, interactions between crystals must be taken into account, which leads to a stronger (exponential or power law) dependence on crystal fraction. At a critical volume fraction ϕ_{max} , the crossover between liquid-like and solid-like rheology is observed. For $\phi < \phi_{\text{max}}$, the relative viscosity is frequently described by the empirical generalization:

$$\eta_{\text{rel}} = (1 - B_E \phi)^n, \quad (28)$$

where $B_E = 1/\phi_{\text{max}}$ and n are adjustable parameters. For close, random, and loose-packed monodispersed spheres, $\phi_{\text{max}} = 0.74, 0.64-0.62$, and $0.6-0.56$ are used, respectively. For random packing of non-spherical crystals (bars, needles) of aspect ratio $\alpha > 10$ ($\alpha = l/d$ with l = length and d = diameter), the equation $\phi_{\text{max}} = 5/\alpha$ holds [51]. For the exponent n , values in the range $-5/2 \leq n \leq -3/2$ are reported such as $n = -5/2$ [52], $n = -4/2$ [53], and $n = -B_E \phi_{\text{max}}$ [54].

For shearing semi-concentrated suspensions with $\phi > 0.3$, the dependences of the relative viscosity on both yield stress and strain rate become evident. The non-Newtonian flow is observed to be of shear thinning type (crystal alignment for non-spherical crystals). Phenomenological equations of the relative viscosity have been proposed to bypass the viscosity divergence of Eq. (28) as $\phi \rightarrow \phi_{\text{max}}$ and to bridge the viscous flow of suspensions with the creep of polycrystalline solids. For a constant strain rate, one finds [55]

$$\eta_{\text{rel}} = \left\{ 1 - A \operatorname{erf} \left(\frac{\sqrt{\pi}}{2} \phi \left[1 + \frac{B}{(1-\phi)^C} \right] \right) \right\}^{-B_E/A} \quad (29)$$

with A, B, C = adjustable parameters.

Experimental data show that for the overall evolution of the relative viscosity with the dispersed volume fraction of rigid crystals, a sigmoidal-shaped increase of up to eight orders of magnitude becomes evident (Figure 17). Its point of inflection, which marks the crossover between liquid-like and solid-like rheology, seems to be specific for each melt and shifts with the aspect ratio and type of packing of the dispersed crystals.

8.3 Bubbly Melts and Emulsions

In contrast to rigid crystal inclusions, the deformability of gas bubbles and liquid droplets (immiscible melts) has to be considered if the deforming (viscosity) forces exceed the retaining (interfacial energy) forces. The equilibrium deformation of a gas bubble and liquid droplet is, therefore, a function of the capillary number:

$$Ca = \frac{\eta_0 r \dot{\epsilon}}{\gamma}, \quad (30)$$

where r is the radius of the bubble or liquid droplet and γ the liquid–gas or liquid–liquid interfacial energy. For bubbly melts and emulsions subjected to steady shear under $Ca > 1$, spherical bubbles (droplets) of volume fraction ϕ will deform, and the apparent viscosity of the melt is predicted to decrease. In contrast, shearing under $Ca < 1$ allows bubbles/droplets to keep their spherical shape and leads to an increase of the apparent viscosity. Empirical equations have been proposed for demixed and bubbly melts of the same type as Eq. (28):

$$\eta_{\text{rel}} = (1 - B_E \phi)^n, \quad (31)$$

where B_E and n are adjustable parameters. Depending on rheometric regime with $Ca > 1$ vs. $Ca < 1$ and the fraction of suspended bubbles (liquids), i.e. dilute vs. semi-concentrated, different values of B_E and n in Eq. (31) have been proposed. In particular for dilute emulsions, linear equations ($n=1$) are proposed such as $B_E=1$ for emulsions under $Ca < 1$ [56], whereas for semi-concentrated emulsions nonlinear equations with $n = -5/2$ and ($B_E=1$ for polydispersed emulsions and $B_E=1.35$ for monodispersed emulsions) are used to fit apparent viscosity data under $Ca < 1$.

Allowing bubble deformation ($Ca > 1$) fits to the experimental data for bubbly silicate melts with volume fractions up to $\approx 62\%$ can be made with $B_E=1$ and $5/3 \leq n \leq 15/3$ (Figure 17). These data show that deformable bubbles can decrease the relative viscosity by up to two orders of magnitude, which is much smaller than the increase caused by rigid crystals.

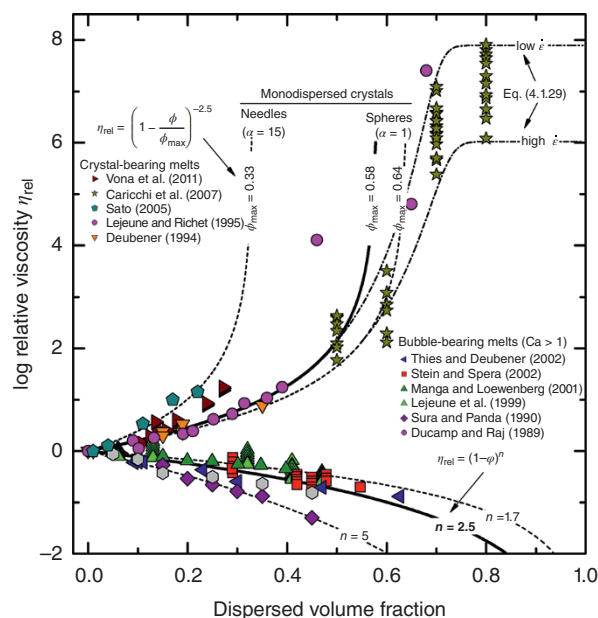


Figure 17 Contrasting effects of the volume fractions of rigid solid inclusions (ϕ) and deformable gas bubbles (ϕ) on the relative viscosity η_{rel} of heterogeneous melts. Crystal-bearing melts, solid line: Eq. (28) for loose-packed monodispersed spheres with $n = -5/2$ and $\phi_{\text{max}} = 0.58$. Bubble-bearing melts, solid line: Eq. (31) for $B_E = 1$ and $n = 5/2$.

9 Perspectives

Viscosity control is essential for glass melting, forming, and cooling, which requires detailed knowledge of the manner in which the rheology depends on temperature and chemical composition and, when inclusions are present in the melt, on their nature and volume fraction. In industry, models have thus been developed for the accurate description of viscosity–composition–temperature relationships from comprehensive databases. In this area, progress will result from industrial and academic research since simulation of dynamic processes is gaining more and more in importance for designing glasses of desired viscous properties. Besides glass industry, geosciences have become a key driver for explaining viscous phenomena with respect to heterogeneity and volatile elements. This expertise will help not only to understand batch and fining processes of glass manufacturing but also engineering of highly viscous composite phases such as glass–polymer hybrids for dental applications and partially crystallized seals for high-temperature fuel cells. From a theoretical standpoint, however, much work remains to be done to understand viscosity at a really fundamental level. The reason, of course, is that viscosity is closely related to the glass transition, which remains itself an elusive phase transformation (Chapter 3.2).

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Appendix

A.1 Supplementary Information

Table 2 From Douglas et al. (1965), Gent (1960), Hagy (1963), Trouton and Andrews (1904).

Figure 3. Division in three viscosity ranges after Nemilov (1992). Data from Sipp et al. (1997, SLS-1), Zeitka and Deubener (2004, SLS-2), De Bast and Gilard (1965, SLS-3), Meinhard et al. (2001, SLS-4), Mazurin et al. (1979, SLS-5), Gerard and Troussard (1951, SLS-6), Jones (1944, SLS-7), and Blaimont et al. (1951, SLS-8).

Figure 4. Data from Martin and Angell (1986, P_2O_5), Urbain et al. (1982, SiO_2), Fontana and Plummer (1966, GeO_2), Napolitano et al. (1965, B_2O_3), Macedo and Napolitano (1968, B_2O_3), Böse et al. (2001, soda-lime-silica, Schott code AR 8350; lead silicate, Schott code LLF1; borosilicate, Schott code 8486), Masuhr et al. (1999, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ – Vitleroy 1), Schröter and Donth (2000, glycerol), Weiler et al. (1969, K, Ca-nitrate), Tweer et al. (1971, K, Ca-nitrate), and Greet and Turnbull (1967, o-terphenyl).

Figure 5. Data sources: E-glass (1) of composition 56.51 SiO_2 , 14.3 Al_2O_3 , 6.40 B_2O_3 , 18.36 CaO , 2.65 MgO , 0.55 FeO , 0.45 Na_2O , 0.35 K_2O , 0.12 TiO_2 (wt %), and 15.91 mol/kg glass with the AG parameter (Eq. 5.6): $A_6 = -3.51$, $B_6 = 2\,670\,200\,J/kg$, $S^{conf}(T_g) = 197.6\,J/kg/K$, $a = 290.02\,J/kg/K$, $b = 0$, $T_g = 996\,K$ (Sipp et al., 1997); E-glass (2): 53.6 SiO_2 , 14.6 Al_2O_3 , 0.3 Fe_2O_3 , 23.5 CaO , 6.3 B_2O_3 , 0.9 Na_2O , 0.7 F_2 (wt %) and 15.81 mol/kg glass with the AG parameter of Eq. (18): $A_6 = -2.65$, $B_6 = 1\,723\,380\,J/kg$, $S^{conf}(T_g) = 126.3\,J/kg/K$, $a = 315\,J/kg/K$, $b = 0$, $T_g = 952\,K$ (Deubener et al., 2008)

Figure 8. Data sources as in Figure 4. Calorimetric T_g ($\tau = 10^2$ seconds) and T_c temperatures are collected from Martin and Angell (1986) and Masuhr et al. (1999) and the compilations of Böhmer et al. (1993), Rössler and Sokolov (1996), [26], Hess et al. (1996), Richert and Angell (1998, [25]) and obtained by fitting the general dependence (indicated by a star in the legend).

Figure 9. Viscosity data from various authors (SciGlass query). Immiscibility dome as calculated from Haller et al. (1974) model with $\Delta S/R = 0.3$, a critical temperature of 1110 K and $(SiO_2)_8$ and $Na_2O \cdot 3SiO_2$ virtual end members.

Figure 10. Viscosity data from various authors (SciGlass query).

Figure 11. Data are from the collections of Eisenberg et al. (1966, [30]), Striepe and Deubener (2012), and Rodrigues and Wondraczek (2014). Glass transition temperature is used when viscosities not reported. For $H(PO_3)$ z/R_{M-O} is set as zero ($T_{12} = 263\,K$) and linear average of z/R_{M-O} is assumed for binary metal mixtures.

Figure 12. Data from Riebling (1966, inverted triangle), Cranmer and Uhlmann (1981, diamond), Toplis et al.

(1997a, box), Toplis et al. (1997b, circle) and Webb et al. (2004, triangle).

Figure 13. Data from the collection of Deubener et al. (2003, [41]) and from Del Gaudio et al. (2007). For hydrous sodium silicate glasses, data of the gel-to-glass transition are included. Glass transition temperature is used if viscosities are not reported. Dashed line gives the prediction of Eq. (22) with $A = 30$ and $B = 5$.

Figure 14. Data collected from Sipp et al. (1997, SLS-1) and Lillie (1933, SLS-2).

Figure 15. Data collected from Simmons et al. (1982, SLS-1 [45]), Yue and Brückner (1994, SLS-2 [46]), Yue and Brückner (1994, SLS-2), and Thies and Deubener (2002, SLS-3).

Figure 16. Data collected for the time to establish equal viscosity in glasses of high and low fictive temperatures (Figure 14) from Lillie (1933, SLS-2, fiber elongation) and Sipp et al. (1997, SLS-1, compression experiments) and for the strain rate to initiate shear thinning from Manns and Brückner (1985, SLS-4, cylinder compression), Simmons et al. (1988, SLS-3, fiber elongation, cone-cup shear), and Yue and Brückner (1994, SLS-5, cylinder compression) as well as for the critical rate to brittle fracture of double-ring bended sheet glasses (SLS-4, Manns and Brückner, 1983).

Figure 17. Crystal-bearing melts: data from Vona (2011), Caricchi et al. (2007), Sato (2005), Lejeune and Richet (1995, [48]), and Deubener (1994). Bubble-bearing melts: Data from Thies and Deubener (2002), Stein and Spera (2002), Manga and Loewenberg (2001), Lejeune et al. (1999, [49]), Sura and Panda (1990), and Ducamp and Raj (1989).

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4.2

Ionic and Electronic Transport

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1 Introduction

Electrical transport in glasses and glass-forming melts is caused by the displacement of mobile charged species, namely, ions and electrons. The existence of ionic conduction in glasses was proved in 1884 by Emil Warburg (1846–1931) [1] who described Na^+ transfer through a thin glass membrane separating two sodium amalgams. Since then, the phenomenon has been put to innumerable uses, thanks in particular to the possibility of enhancing conductivity through optimization of the chemical composition of the material. To give a single example, substitution of sulfur for oxygen in lithium-bearing glasses causes the conductivity to reach a value of about $10^{-3} \text{ S cm}^{-1}$ at room temperature, which is similar to those of liquid electrolyte solutions, whence the use of these materials as electrolytes in secondary solid-state lithium cells ([2, 3], Chapter 9.5).

In a general way, ionic conductivities vary with temperature according to Arrhenius laws up to the glass transition and show the highest values for glasses and melts bearing singly charged cations such as Li^+ , Na^+ , or Ag^+ . Since ionic transport makes it possible to modify the chemical composition of the glass surface, it is, for instance, used industrially to strengthen glass by ion stuffing (see Chapter 3.12) or to obtain index gradients in optical guides. In addition, ion conductive glasses are currently used as active membranes for electrochemical devices, as pH or ion selective electrodes (Chapter 5.8), whereas ionic conduction also plays a fundamental role in redox reactions in melts (Chapter 5.6, [4]). As will be first described in this chapter, a comprehensive

understanding of ionic transport associates concepts already developed in the field of ionic crystals, electrolytic solutions, molten salts, and thermodynamics.

When transition elements are present in at least two redox states, electrical conduction can also take place in a large variety of glasses by tunneling electron transfer between localized donor and acceptor states energetically located between the valence and conduction bands. Although electronic conduction also follows Arrhenius laws below the glass transition, its mechanisms are thus completely different from those of ionic transport. Following the pioneering approach developed by Mott [5] in the 1960s, electronically conductive glasses have been studied for more than 50 years. In the last two decades, they have even been more extensively investigated than ionic conductive glasses because of their high-tech applications. For instance, Se or As–Se photoconductive chalcogenide glasses have enabled the photocopying process to be developed, whereas electronic conduction in amorphous hydrogenated silicon, a-Si:H, has boosted production of low-cost solar cells [6]. In addition, electronically conductive amorphous phases of transition metal oxides such as WO_3 , MoO_3 , and glassy systems containing V, Fe, Mo, or Cu oxides associated with glass formers such as SiO_2 , P_2O_5 , and TeO_2 have been studied for applications as electrochromic coating for “smart windows” or electrode materials in lithium batteries.

If subjected to a high electric field, electronically conductive glasses may eventually switch reversibly from low to high conductivity, a property that is now exploited in electrical memory devices for information storage [7]. As will be seen in the second part of this chapter, theoretical studies of electronic conductivity, as well as the corresponding terminology, derive from usual concepts of solid-state physics. This is why electronic conductive glasses have been most studied by the physics community.

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2 Ionic Conductivity and Diffusion

2.1 Experimental Determination

The ionic conductivity, σ_i , is readily determined from the electrical resistance R_i of a sample between two parallel metallic electrodes of surface S mutually separated by a distance d : $\sigma_i = \frac{1}{R_i} \times \frac{d}{S}$.

From an experimental point of view, the major difficulty arises from the fact that the sample is an ionic conductor, whereas the electrodes are electronic conductors. Hence, there is an irreversible energy loss caused by charge transfer at the sample/electrode interface, which is represented by a resistance R_{tr} in series with the sample resistance. To separate these two resistances, the usual technique is to perform ac impedance measurements in the 10 Hz to 1 MHz range. A representation of the impedance Z^* in the complex plane then enables one to separate the bulk response from that of the glass/electrode interface and to determine accurately R_b and σ_i .

If no transfer resistance were existing at the glass/electrode interface, the electrical conductivity could be measured from direct current (dc) measurements. For this reason σ_i is often ambiguously called dc conductivity (σ_{dc}) even though it is actually determined from ac measurements. As usually expressed in $S\text{ cm}^{-1}$ or $\Omega^{-1}\text{ cm}^{-1}$, the ionic conductivity of window glass typically ranges from 10^{-15} to $10^{-13}\text{ S cm}^{-1}$ at room temperature, which is why glasses are usually considered as insulators at room temperature. Such low values are more conveniently expressed in terms of resistivity $\rho = 1/\sigma$.

The highest ionic conductivities are observed when monovalent cations such as alkalis are present in the glass. Compared with that of alkalis, the contribution of cations having a higher positive charge, such as Ca^{2+} or Pb^{2+} , is much lower because, at a similar cation concentration, they are more tightly bonded to the anionic framework, causing their room-temperature conductivity to be lower by five to eight orders of magnitude. Consequently, the majority of conductivity data and theoretical approaches deal with monovalent cations.

The ionic conductivity, σ_i , and the diffusion coefficient, D_i , of a monovalent cation are linked by the Nernst-Einstein proportionality relationship:

$$\sigma_i = \frac{xe^2 D_i}{k_B T}, \quad (1)$$

in which x is the cation concentration, T is the absolute temperature, and e and k_B are the electron charge and Boltzmann constant. This relationship simply assumes that ionic transport and diffusion are governed by the same mechanism, whatever the “driving force,” electric field, or concentration gradient may be.

2.2 Temperature Dependence of Ionic Conductivity

Below the glass transition, the ionic conductivity increases exponentially with temperature to follow an Arrhenius law:

$$\sigma_i = \frac{A_i}{T} \exp\left(-\frac{E_a}{k_B T}\right), \quad (2)$$

where E_a is the activation energy, which usually ranges from 0.5 to 1.5 eV (i.e. approximately 50 and 150 kJ mol^{-1}), and where the constant A_i does not significantly depend on glass composition with values of 10^4 – 10^5 K S cm^{-1} . This feature means that conductivities extrapolated at infinite temperature would converge to a common value. The conductivity differences of about 10 orders of magnitude observed at room temperature (typically from 10^{-17} to 10^{-7} S cm^{-1}) are thus due to variations in the $E_a/k_B T$ rather than to the pre-exponential A_i/T term. For alkali and alkaline earth, conductive glasses, E_a ranges between 0.6 to 1 eV and between 1.3 and 1.7 eV, respectively [8]. Up to the glass transition these variations of A_i/T over intervals of a few hundred degrees are actually small enough that one generally prefers the alternate equation

$$\sigma_i = \sigma_{0i} \exp\left(-\frac{E_a}{k_B T}\right). \quad (3)$$

Above the glass transition, the ionic conductivity dependence with temperature is no more Arrhenian and increases faster with temperature. Like those of viscosity, however, its variations cannot be represented by Eq. (2) or (3) as illustrated in Figure 1 for two sodium

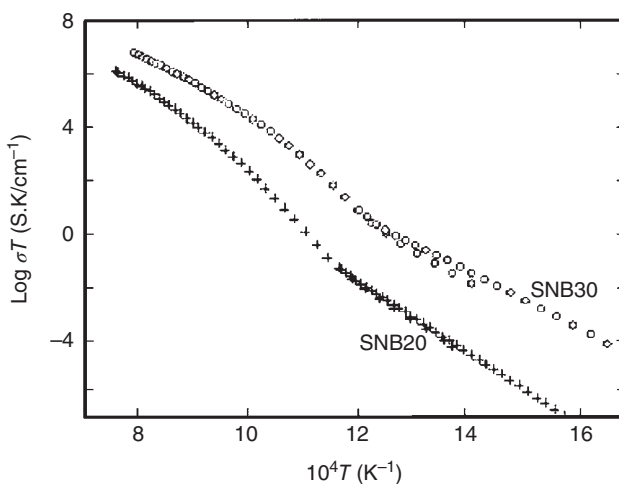
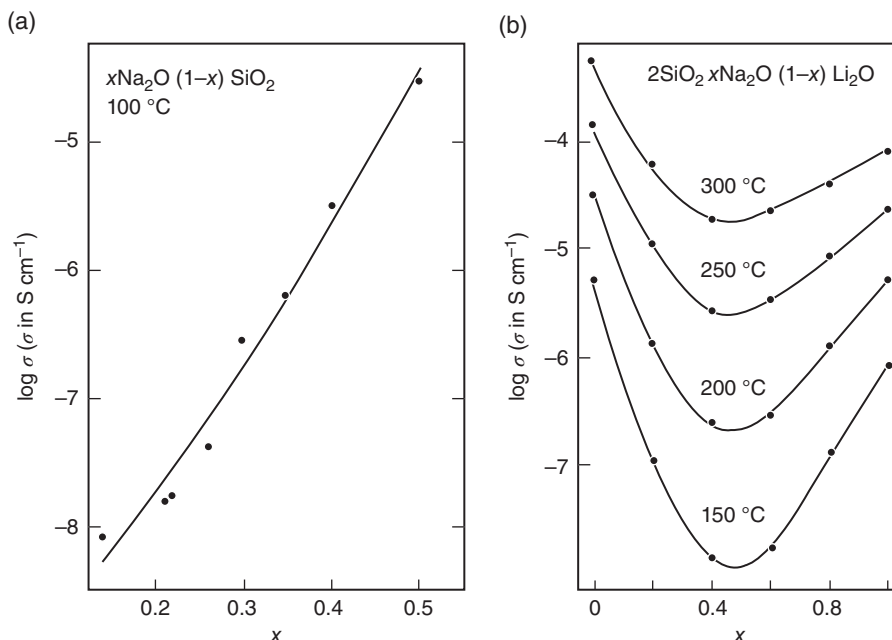


Figure 1 Contrast between the Arrhenian and non-Arrhenian regimes of the low- and high-temperature ionic conductivity for two glass-forming melts with 20, 25, and 55 (SBN20) and 30, 22, and 48 (SBN30) mol % Na_2O , B_2O_3 , and SiO_2 , respectively, illustrating how cooperative motion of the borosilicate chains enhance the mobility of charge carriers.

Figure 2 Composition dependence of the ionic conductivity in alkali silicate glasses. (a) Effect of the ($\text{Na}_2\text{O}, \text{SiO}_2$) substitution at 100 °C. (b) Mixed alkali effect at temperatures from 150 to 300 °C resulting from (Na, Li) substitution in disilicate glasses.



borosilicate glass forming melts [9]. Above 1300 °C, glass-forming melts even reach very high ionic conductivities of about $10^{-2} \text{ S cm}^{-1}$, which are similar to those found for strong aqueous electrolyte solutions. As a matter of fact, it is this ionic-resistor character that makes it possible to increase (boost) the temperature of a glass-forming melt by Joule heating with immersed molybdenum electrodes (Chapter 9.7).

2.3 Composition Dependence of Ionic Conductivity

Ionic transport is highly sensitive not only to temperature but also to the nature and concentration, x , of the moving cations. In alkali silicates, doubling x , for instance, induces a 10- to 100-fold increase in conductivity. This sensitivity to chemical composition is spectacularly illustrated by the mixed alkali effect (Chapter 4.6, [10, 11]). At a constant concentration of alkali cations, the progressive substitution of an alkali by another results in a marked decrease in the ionic conductivity, compared with that of glasses containing only one alkali, which becomes even stronger when the temperature decreases (Figure 2).

3 Ionic Transport Mechanisms

3.1 General Features

Regardless of any particular mechanism, electrical transport can be expressed as the product of the concentration

of effective charge carriers, x_e , their mobility, μ_i , and electrical charge, e_i . In the simplest case of a positively charged monovalent cation, the ionic conductivity, σ_i , then is

$$\sigma_i = e \cdot x_e \cdot \mu_i. \quad (4)$$

In electrolyte solutions or ionic conductive crystals, the concentration x_e of effective charge carriers is the mean concentration of the ions actually moving. Usually, it is expressed as the number of charge carriers by cm^{-3} so that ion mobilities are reported in $\text{cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, which represents the speed of charge carriers in cm s^{-1} when subjected to an electric field of 1 V cm^{-1} . In any case, it is generally admitted that $x_e \ll x$, which does not mean that some cations will never move, but only that, statistically, a small fraction of all cations move at any given time. At equilibrium, however, a continuous exchange takes place such that each cation is alternatively an effective charge carrier or is trapped in a fixed position (Chapter 4.6). Below the glass transition, alkali cations move in a frozen network. Ionic transport in glasses thus is usually interpreted in terms of the vacancy or indirect interstitial mechanisms described for ionic crystals. Above the glass transition, in contrast, cations no longer move in a frozen network. The rearranging structural entities of the melt participate in cation displacements so that conduction mechanism become comparable to those of molten salts or ionic polymers. The various mechanisms proposed for these low- and high-temperature regimes will now be described in some detail.

3.2 Ionic Transport Below the Glass Transition: The Ionic Crystal Formalism

3.2.1 Anderson–Stuart Model: A Vacancy Mechanism

This model [12] mainly serves to estimate the activation energy for ionic migration, E_a , from classical electrostatic and elasticity theories. Its mechanism is similar to that of vacancy formation because it assumes the presence of a large number of available cation sites, but does not distinguish between bridging and nonbridging oxygens and posits that all the constituents of the material are in an ionic form. Then the basic idea is that an ion makes a simple hop from one site to another, passing through a “doorway” that opens to the size of the ion as it passes through. As a result, the activation energy E_a is the sum of two terms, the electrostatic binding energy, E_B , and the strain energy, E_S , required to move an ion from one site to another. Because the anion–cation distance increases with cation size, the ionic binding energy correlatively decreases and the strain energy increases. In the expression of the activation energy $E_a = E_B + E_S$, the two terms compete, and for a given glass structure, the activation energy is expected to present a minimum as a function of the cation size. For alkali and alkaline earth silicate glasses, this minimum is found for Na^+ and Sr^{2+} , respectively. Despite its simplicity, this model yields the right orders of magnitude for activation energies and their dependence on cation size.

3.2.2 An Improved Vacancy Mechanism: The Dynamic Structure Model

In single M^+ cation conductive glasses, the model proposed by Bunde, Ingram, and Maass [13] relates the ionic conductivity and its activation energy to the concentration of the network modifier oxide, M_2O . When trapped in a regular cationic site, an M^+ cation induces a local deformation of the surrounding glass network as a result of its positive charge and size. To some extent, the cation can be compared with a polaron in an ionic crystal, in which the local structure adapts to a trapped electron. When the M^+ cation jumps out of its site, this associated local deformation relaxes toward a new equilibrium state, preserving the “memory” of this local deformation for some time. The moving M^+ cation may then either create a new cationic site adapted to its charge and radius or jump into a relaxing empty cationic site. Owing to the energy cost required to create a new local reorganization, the activation energy for the jump is higher in the first event and makes this first step less probable than the second.

With Monte Carlo computational simulations (Chapter 2.8), one can show that cationic sites tend to form fluctuating clusters whose size increases as a function of the M_2O concentration or temperature. These

clusters percolate through cationic pathways, enabling cations to migrate in the glass. The ionic conductivity calculated by this procedure accounts for the strong dependence of ionic conductivity on composition (Figure 2a) and reproduces the experimentally observed logarithmic decrease of E_a with alkali oxide content. Such a model also yields a satisfactory interpretation of the mixed alkali effect (Figure 2b) if extended to two different alkali charge carriers, each generating a different cationic site.

3.2.3 Charles Model: An Interstitial Pair Mechanism

This mechanism assumes that the charge carriers are cation pairs composed of two alkalis sharing the same equilibrium site [14]. In an oxide glass, an equilibrium site could be a negatively charged nonbridging oxygen bonded to a cation. Such a neutral association is all the more stable that the relative dielectric constant ϵ_r of an oxide glass is low, ranging typically between 5 and 15 [8]. Nevertheless, thermal vibrations allow for partial dissociation so that some alkali cations escape from the electrostatic attraction of their nonbridging oxygens and jump into the potential well of a neighboring oxygen already occupied by another alkali cation. The cationic pair thus created forms a positive charge carrier (Figure 3a), which can be considered as a defect from an electrostatic standpoint. Being unstable, the cationic pair expels an alkali to a neighboring nonbridging oxygen already associated with another alkali cation, and so on. Each time a cation pair is formed it migrates along the electric field from one nonbridging oxygen to another (Figure 3b). Implying an exchange in coordination number between two neighboring nonbridging oxygens, this mechanism can be compared to the transfer of protons in water from a H_3O^+ hydronium ion to a H_2O molecule by a mechanism originally described by Theodor von Grotthuss (1785–1822) [15].

3.2.4 Mechanisms Inferred from Diffusion Measurements

For an ionic crystal, and also for a glass, the diffusion coefficient of an element, D_i^* , determined by radiotracer experiments is slightly lower than D_i , deduced with the Nernst–Einstein equation (1) from conductivity data. This difference is expressed by $D_i^* = H_R D_i$, where H_R is the Haven ratio. In a crystalline ionic conductor, in which ions follow a random walk as in a direct interstitial process, H_R is expected to be unity. If some jumps are precluded after a given jump, the Haven ratio depends on the number Z of neighboring sites, being approximated by $H_R = [1 - 2/Z]$ for a vacancy mechanism and by $H_R = [1 - (1/Z)]$ for an indirect interstitial process. Because Z depends on crystal structure, a determination

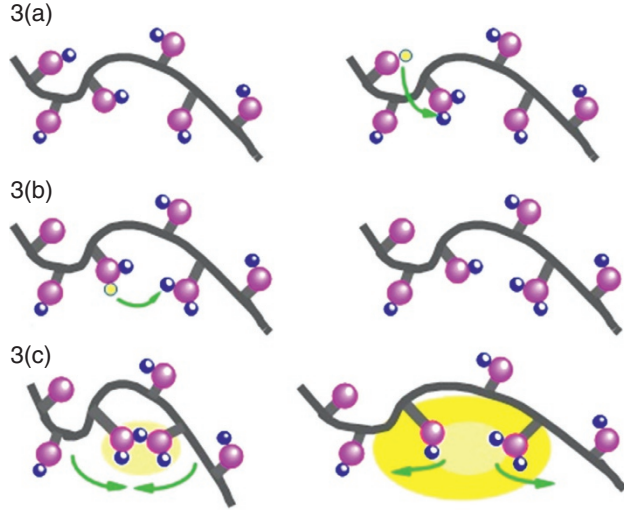


Figure 3 Possible ionic transport mechanisms. (a) Formation of an interstitial pair by an activated process. (b) Interstitial pair migration by an activated mechanism below the glass transition. (c) Interstitial pair migration by an entropic mechanism involving cooperative chain movements above the glass transition.

of H_R enables these transport mechanism to be distinguished.

In a glass, the local structure, and hence Z , is not well defined, and the determination of H_R is less conclusive. For silicate glasses with high Na^+ contents, the values found for H_R range from 0.44 to 0.55 and tend toward unity at low contents [16, 17]. From Charles model [14], one assumes that the cationic interstitial sites consist of many equivalent positions around a nonbridging oxygen already associated with another cation. At very low Na^+ concentrations, diffusive motion would occur by a direct interstitial mechanism between different nonbridging oxygens.

3.2.5 More About the Ionic Crystal Formalism

Starting from the interstitial pair model, one readily extends the classical defect model to glasses [18] and, in this way, accounts for the Arrhenian variations of ionic transport, i.e. Eq. (2) or (3). Assuming that charge carriers are formed in glasses through an activated process, one expresses their concentration as

$$x_e = x \exp \left(- \frac{\Delta G_f}{2k_B T} \right), \quad (5)$$

where $\Delta G_f = \Delta H_f - T\Delta S_f$ is the Gibbs free energy associated with the simultaneous formation of an interstitial pair and a cationic “vacancy” and ΔH_f and ΔS_f are their formation enthalpy and entropy, respectively. As for the factor 2 in the exponent, it expresses the fact that the

process generates two charged species, a charge carrier and its vacant site, both in the same amounts.

Using the Nernst–Einstein equation (1), one expresses the mobility of the charge carriers as a function of their diffusion coefficients D_i and then as a function of their characteristic attempt frequency, ν , and jump distance, λ :

$$\mu_i = \frac{eD_i}{k_B T} = \frac{e\lambda^2\nu}{6k_B T} \Omega, \quad (6)$$

where Ω is the probability of a successful jump. For a thermally activated mechanism, $\Omega = \Omega_1$ with a value that is a function of the Gibbs free energy required for migration, ΔG_m :

$$\Omega = \Omega_1 = \exp \left(- \frac{\Delta G_m}{k_B T} \right). \quad (7)$$

Finally, the following expression can be proposed for the cationic conductivity:

$$\sigma_i = ex_e\mu_i = x \frac{e^2\lambda^2\nu}{6k_B T} \exp \left(- \frac{\Delta G_f/2 + \Delta G_m}{k_B T} \right), \quad (8)$$

or, after separation of the enthalpic and entropic terms:

$$\sigma_i = x \frac{e^2\lambda^2\nu}{6k_B T} \exp \left(\frac{\Delta S_f/2 + \Delta S_m}{k_B} \right) \exp \left(- \frac{\Delta H_f/2 + \Delta H_m}{k_B T} \right). \quad (9)$$

Because this relationship is of the same form as the experimentally observed Arrhenius law, identification with Eq. (2) yields the parameter E_A as

$$E_A = \Delta H_f/2 + \Delta H_m, \quad (10)$$

and the temperature-independent term A_i as

$$A_i = x \frac{e^2\lambda^2\nu}{6k_B} \exp \left(\frac{\Delta S_f/2 + \Delta S_m}{k_B} \right). \quad (11)$$

The pre-exponential term $xe^2\lambda^2\nu/6k_B$ can be assessed numerically from realistic values of density and far infrared data, namely, $x = 10^{22}$ ions cm^{-3} , $\lambda = \sqrt[3]{1/x}$, and $\nu = 10^{13}$ Hz, yielding $A_i \approx 10^5$ K S cm^{-1} , which is close to typical experimental values. Consequently, either the exponential term in Eq. (11) is close to unity or the entropy terms are very low compared with k_B . This means that charge carrier formation and migration do not induce a significant change in the local order, as it would be expected from a rigid macromolecular network below the glass transition temperature.

3.2.6 Ionic Transport and Pressure

Most ionic conductivity data are presented as a function of composition and temperature. Complementary information can be deduced from the pressure dependence

of the conductivity variations as measured under isostatic conditions when a glass sample is immersed in an insulating oil between 1 and 5000 bar [19, 20]. A significant decrease in ionic conductivity is observed, which can be converted into an activation volume.

Because $xe^2\lambda^2\nu$ can be considered constant, one determines the pressure dependence of the conductivity by differentiation of Eq. (8):

$$\left(\frac{\partial \ln \sigma_i}{\partial P}\right)_T = -\frac{1}{k_B T} \left(\frac{\partial(\Delta G_f/2 + \Delta G_m)}{\partial P}\right)_T. \quad (12)$$

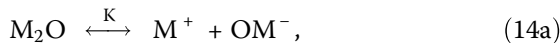
Then, since $d\Delta G = \Delta V dP - \Delta S dT$, Eq. (12) can be rewritten as

$$\Delta V_f/2 + \Delta V_m = \Delta V_a = -k_B T \left(\frac{\partial \ln \sigma_i}{\partial P}\right)_T, \quad (13)$$

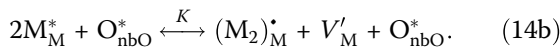
where ΔV_a is an activation volume, i.e. the local variation of volume necessary for the formation and displacement of a charge carrier. Experimentally, one finds that the activation volume is close to the estimated ionic volume calculated from the Goldschmidt radius of the positive cation causing ionic transport.

3.2.7 The Weak Electrolyte Model

Ravaine and Souquet [21] extended the concept of weak electrolyte solutions to glassy electrolytes in order to interpret the huge variations observed in ionic conductivity as a function of the total alkali ion concentration (Figure 2a). Basically, the charge carrier mobility μ_i is expected to remain constant at a constant temperature for a given glass former. The number of charge carriers would then result from the partial dissociation of the modifier in a solvent of low dielectric constant, which is the glass former. In the simple case of a M_2O - SiO_2 binary glass, where M is an alkali cation, the dissociation equilibrium is



with Kröger–Vink notation, which allows for clearer identification of the species, assuming an interstitial pair formation ($2M^*$) as a charge carrier, which could be a nonbridging oxygen associated to two alkali cations (Figure 3a):



The equilibrium constant associated with the dissociation reaction (14) is

$$K = \exp\left(\frac{-\Delta G_f^0}{k_B T}\right), \quad (15)$$

where ΔG_f^0 is the standard Gibbs free energy of dissociation relevant to a specific composition. For high values of

ΔG_f^0 , K is very low so that there are far fewer effective charge carriers than alkali cations. At a constant temperature, but for different M_2O amounts, the number of effective charge carriers can be written as

$$x_e = x \exp\left(\frac{\Delta G_f^0 + \Delta \bar{G}_{M_2O}}{2k_B T}\right), \quad (16)$$

where $\Delta \bar{G}_{M_2O}$ is the chemical potential of M_2O in the chosen reference state and in the glass under study. Finally, since the mobility term is considered constant, the variations in ionic conductivity with composition follow the variations in the partial free energy of the alkali oxide, according to

$$\log \sigma_i \propto \log x_e \propto \frac{\Delta \bar{G}_{M_2O}}{2k_B T}. \quad (17)$$

Thus, the considerable variations observed in conductivity are representative of the significant variations with composition of the chemical potential of the alkali oxide. In a further step, one can interpret these variations by applying to glasses usual thermodynamic formalisms such as the regular or quasi-chemical models (Chapter 5.3).

4 Ionic Transport Above the Glass Transition: An Entropic Mechanism

As already noted, above the glass transition the rearranging structural entities of the melt participate in the cationic displacement so that conduction mechanisms become comparable to those in molten salts or ionic polymers [22, 23]. Under these circumstances, the ionic conductivity of a melt is higher than the values extrapolated from the Arrhenius law for the glass. This difference points to the existence of other modes of transport in addition to the aforementioned activated migration mechanism. This high-temperature process, represented schematically in Figure 3c, is associated with the local movement of the network-forming macromolecular chains. In this process, the transfer of the interstitial pair is no longer “drawn out” from the mean thermal energy $k_B T$ but from the available configurational entropy [24] associated with the chain movements.

In a supercooled glass-forming liquid, this configurational entropy decreases with temperature and would disappear at the *ideal* glass transition temperature, T_0 (Chapter 3.3, [25, 26]). As estimated by extrapolation from the thermodynamic or dynamic characteristics of the supercooled liquid, this temperature is much lower than the glass transition temperature as, for instance, determined by differential scanning calorimetry ($T_g \cong 1.3 T_0$).

The probability of a charge carrier transfer by such an entropic process depends on the available configurational entropy, and consequently on T_0 , and is expressed by

$$\Omega_2 = \exp \left(- \frac{B}{k_B(T - T_0)} \right), \quad (18)$$

where B is an energy dimension constant.

According to the present model, the moving species is in this case an interstitial pair transferred from one non-bridging oxygen site to another, allowing for charge transfer in the glass network. Above T_0 , the charge transfer may occur either by an activated jump (Ω_1) or by an entropic mechanism (Ω_2), and the total jump probability Ω is given by

$$\Omega = \Omega_1 + \Omega_2(1 - \Omega_1), \quad (19)$$

which suggests that the entropic process, Ω_2 , only applies to the unsuccessful first (activated) process, Ω_1 . Under these conditions, the cationic conductivity becomes

$$\sigma_i T = x \frac{e^2 \lambda^2 \nu}{6k_B} \exp \left(- \frac{\Delta G_f/2}{k_B T} \right) [\Omega_1 + \Omega_2(1 - \Omega_1)]. \quad (20)$$

At temperatures slightly higher than the glass transition, the two mechanisms participate in charge carrier mobility, leading to a deviation from an Arrhenius law. At higher temperatures, Ω_2 is expected to prevail over Ω_1 and Eq. (18) thus becomes

$$\sigma_i T = x \frac{e^2 \lambda^2 \nu}{6k_B} \exp \left(- \frac{\Delta G_f/2}{k_B T} \right) \exp \left(- \frac{B}{k_B(T - T_0)} \right), \quad (21)$$

which accounts for the nonlinear variations of the $\sigma_i T$ product in an Arrhenius plot (Figure 1).

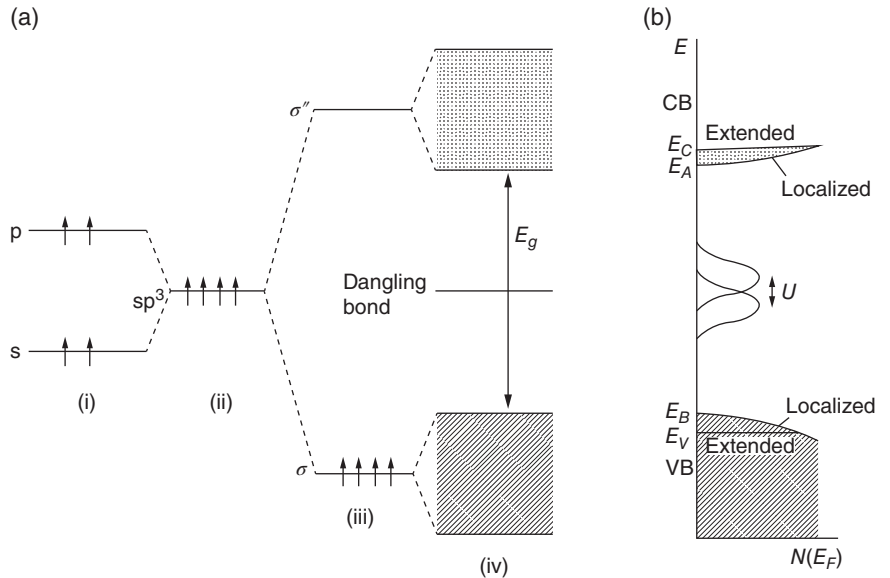
5 Electronically Conductive Glasses

5.1 Band Scheme and Localized States in Covalent or Ionic Glasses

Amorphous silicon is a good example to summarize the main features of bonding relevant to electron conduction in oxide glasses. In this material, Si atoms are linked to four other atoms by four σ_{sp^3} covalent bonds of the valence band. The empty conduction band is formed from the empty antibonding $\sigma_{sp^3}^*$ orbitals. Owing to the distributions of bonds angles or bond lengths, the limits of the valence band and conduction band are less well defined than in a crystal, and some “band tails” of localized states slightly reduce the band gap energy. When disorder is more significant, bonds between two silicon atoms are broken and form free sp^3 atomic orbitals, also called dangling bonds D. Each dangling bond may contain zero, one, or two electrons, forming the D^+ , D^0 , and D^- electronic defects, respectively. A donor state would be a D^- dangling bond susceptible to lose an electron to a D^+ or D^0 acceptor site. As sketched in Figure 4, these dangling bonds are localized in the middle of the band gap, where they fix the Fermi level.

Electronically conductive oxide glasses bearing transition metals represent another example of an electronic transport through localized states in the band gap. According to a simplified ionic description of a silicate glass, the valence band would be an O^{2-} full p band,

Figure 4 Band scheme for amorphous silicon. (a) Origin of valence and conduction band states. (b) Associated density of states. Note the dangling bonds band fixing the Fermi level near midgap. Source: Sketched from Elliott [27].



and the conduction band an empty sp^3 band of Si^{4+} . When transition metal (M) oxides are incorporated in the glass structure, they are usually found in different oxidation states, M^{n+} and M^{n+1} , which introduce localized donor (M^{n+1}) and acceptor (M^{n+}) states in the band gap and pin the Fermi level.

5.2 Temperature Dependence of Electronic Conductivity

The techniques used to measure electronic conductivity do not need to be described as they are basically the same as for ionic conductivity. Because electron transfer at the electronically conductive glass/electrode interface is less energy dissipative, however, dc techniques simpler than impedance measurements can be used. When the temperature is increased from ambient conditions, one then finds that the variations of the electronic conductivity, σ_e , is described by equations similar to those presented for ionic conductive glasses, Eqs. (2) and (3):

$$\sigma_e = \frac{A_e}{T} \exp\left(-\frac{E_a}{k_B T}\right). \quad (22)$$

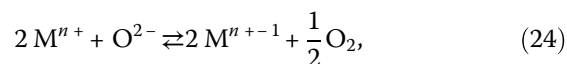
On the other hand, much below room temperature (Figure 5), the exponential dependence of conductivity tends progressively toward

$$\sigma_e \propto \exp\left(-\frac{B}{T^{1/4}}\right). \quad (23)$$

The exponent $1/4$ is the reciprocal of the effective dimensionality for the electronic transfer. An electron can jump only when two sites are close in the four coordinate space x, y, z, E .

5.3 Possible Electronic Transport Mechanisms

In oxide glasses, electronic displacements occur by electron transfer between two oxidation states of a given transition metal M. These two states, M^{n+} and M^{n+1} , result from redox reactions during glass synthesis involving oxygen from the atmosphere or other reservoir:



a reaction whose equilibrium constant depends on temperature, pressure, and chemical composition (Chapter 5.6). After quenching, the kinetics of the redox reaction are exceedingly sluggish so that the relative concentrations of the two valence states remain constant. Electronic conductivity then proceeds by successive electron transfer between the two oxidation states. Obviously, the probability that such a transfer occurs is greater when the two oxidation states are present in comparable concentrations. For this reason, vanadium oxide-based glasses have been studied more extensively, since, under usual synthesis conditions in air, the two valence states, V^{+IV} (d^1 configuration) and V^{+V} (d^0 configuration), have similar concentrations.

In its reduced state, the transition metal cation (M^{n+1}) has by definition a lower positive charge than in its oxidized state (M^{n+}). Consequently, the neighboring negatively charged oxygen anions are less attracted and at a greater distance than in the oxidized form. This local distortion and the electron that create it are called a “polaron,” a quasiparticle to which is thus associated a wave function. When this local distortion does not extend over the first neighboring atoms, the polaron is designated as “small,” which is the usual case for oxide

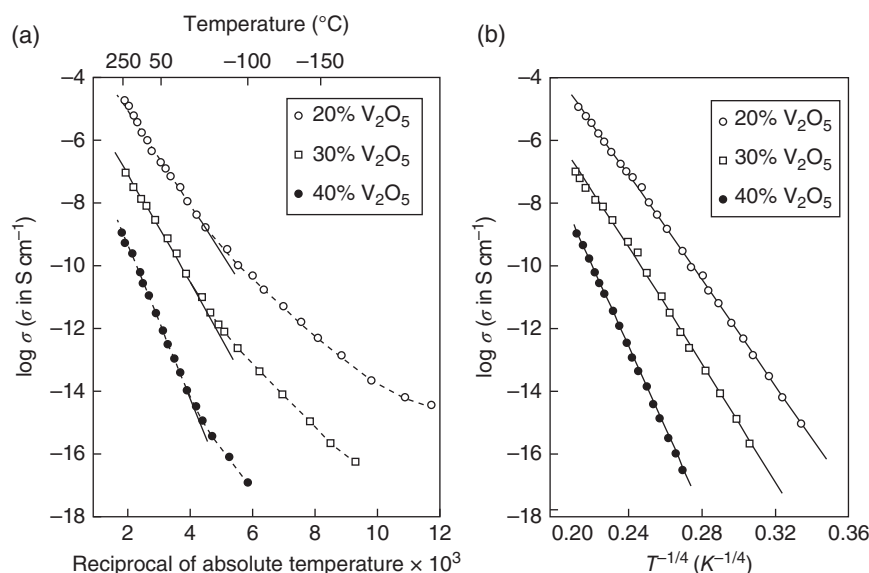


Figure 5 Electronic conductivity of three V_2O_5 - TeO_2 - Bi_2O_3 glasses as a function of temperature for the mole fractions indicated [28]. (a) Conductivity increases with increasing V_2O_5 molar ratio, fits being made to the data with Arrhenius equation (22). (b) Linear plots of the same dc data against $T^{-1/4}$, consistent with the variable range hopping Eq. (23).

glasses. The small polaron may be transferred from the reduced to the oxidized form of the transition metal cation by different mechanisms at high and low temperatures.

At high temperatures – typically $T > \Theta/2$ where Θ is the Debye temperature ($\Theta = 500$ K for SiO_2 glass) – lattice vibrations cause the surroundings of the donor and acceptor sites to have, temporarily, the same energies so that only electrons are transferred by tunneling from the reduced to a neighboring oxidized valences (Figure 6). In an intermediate state (Figure 6b), the electron is delocalized between the two metal cations. This electron delocalization can be also seen as the formation of a molecular orbital (Figure 7) between the d orbitals of two vanadium ions, for instance, and the p orbital of a bridging oxygen. A binding energy J is associated with the formation of this transition state, and the total energy required for the electron transfer can be written as $E_a = 1/2W_p - J$, where $1/2W_p$ is the energy provided by the lattice

to equalize the energy levels of both donor and acceptor sites.

With this approach, Mott and Davis [29] derived the following expression for electronic conductivity:

$$\sigma_e T = x \frac{e^2 \lambda^2 \nu_p}{k_B} y(1-y) \exp(-2\alpha\lambda) \exp\left(-\frac{E_a}{k_B T}\right), \quad (25)$$

where x is the total concentration of the transition metal, ν_p the phonon frequency giving rise to the equalization of the energy levels of the donor and acceptor sites, λ the distance between two neighboring sites, y the molar ratio of the reduced form, and α the exponential electronic decay of the d orbitals. This expression can be seen as the product of three probabilities: (i) the $y(1-y)$ term, which is the probability of finding an acceptor site close to a donor site; (ii) $\exp(-2\alpha\lambda)$, that of an electronic transfer occurring between two adjacent sites; and (iii) $\exp(-E_a/k_B T)$, that of locally providing the energy necessary to form the transition state. All the temperature-independent terms can be gathered in a single A_e term, namely,

$$A_e = x \frac{e^2 \lambda^2 \nu_p}{k_B} y(1-y) \exp(-2\alpha\lambda). \quad (26)$$

Within a limited range of temperatures, this expression accounts for the experimental results represented by Eq. (22) where activation energies (E_a) range from 0.3 to 0.5 eV and the pre-exponential term (A_e) from 10 to 10^2 K S cm $^{-1}$, being lower than in ionic conductive glasses.

At low temperature, typically for $T < \Theta/2$, the electron and the associated local deformation may move simultaneously by tunneling from the donor (M^{n+1}) to an acceptor (M^{n+}) site. Physically, this means that the mean thermal energy $k_B T$ is too low for the activation energy

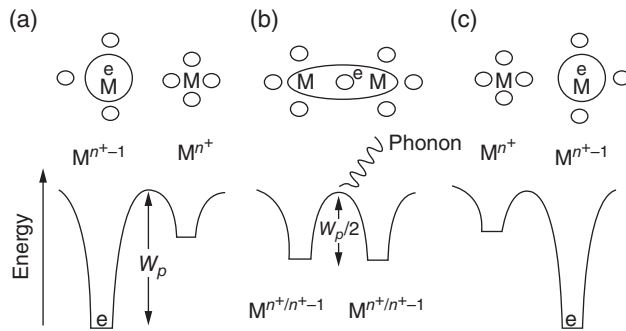
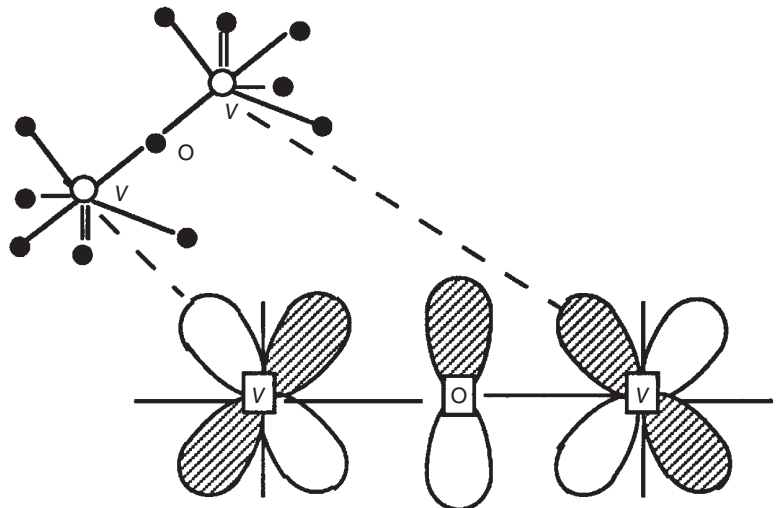


Figure 6 Sketch of electron hopping by a phonon-assisted tunneling process. (a) Before hopping. (b) Phonon-activated transition state. (c) After hopping.

Figure 7 Electronic delocalization during electron transfer between two vanadium cations, implying the formation of π bonds between the d orbitals of vanadium cations and a p orbital of a bridging oxygen.



E_a to be overcome locally so that tunneling transfer may occur over several interatomic distances, i.e. at a distance $R \gg \lambda$, until an acceptor site with a similar energy is found for the donor site. Mott called this process “variable range hopping” [29] and estimated R as a function of temperature and $N(E_F)$, the density of states near the Fermi level, to be

$$R \approx [\alpha k_B T N(E_F)]^{-\frac{1}{4}}. \quad (27)$$

At low temperatures, this expression thus describes the temperature dependence of conductivity as expressed by Eq. (21).

5.4 Electronic Switching Effect in Oxide and Chalcogenide Glasses

Although attention has been paid in this chapter to oxide glasses, the basic concepts presented apply to other classes of glasses as well. Covalent and chalcogenide glasses are cases in point with their electronic conductivity occurring by means of electron transfer between localized states in the band gap, which is phonon assisted over $\Theta/2$, and by a variable range hopping below this value. Of particular interest is the “switching effect,” originally described by Ovshinsky [30] in 1968 on a Te–As–Si–Ge glass, which consists of a sudden increase in the electronic conductivity of the glass, by up to six to eight orders of magnitude, in response to the application of a sufficiently high electric field. Such a switch was later observed in a large variety of chalcogenide and also in oxide-based glasses. Between the conductive (“on”) and resistive (“off”) states, the effect is very fast as it takes less than 10^{-9} s and it is also reversible, currently over 10^{10} cycles. It is thus actively studied, mainly for the storage of binary information. Two main mechanisms have been identified.

The first, the threshold switch, is considered to be a pure electronic mechanism [31]. The localized states in a glass pin the Fermi level near the center of the gap and provide the high resistance of the “off” states described in Section 2.2. Under an electric field of about 10^5 V cm $^{-1}$, the injected electrons and holes from the electrodes fill the empty localized levels and generate a conductive plasma made of a degenerate electron and hole gas. A high electronic conductivity (“on” state) appears, called the threshold switch. This conductive state returns to the resistive state below a minimum value of the applied voltage, the *holding* voltage.

The second mechanism is called memory switch [7]. In this case, local Joule heating brings about controlled and reversible precipitation of a crystalline phase of much higher electronic conductivity than that of the glass. The “off” to “on” transition results from heating the glass

to just above T_g , where fast crystallization produces conducting paths in the form of filaments forming throughout the thickness of the film. The current pulse then causes the reverse transition to take place through melting of the filaments. By heat loss to the surrounding material, the molten filaments are quickly quenched to the original glass phase, returning the film to the low conductive “off” state. In this case, the “on” state does not need a holding voltage to store the information. Commercial memories based on these properties are called phase change memories (PCM). They are currently able to store up to 512 Mbits on a simple chip. In this case, glass compositions are chosen to allow for devitrification with low structural cross-linking as $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$ or $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloys [31].

6 Perspectives

The main characteristics of ionic transport are its high sensitivities to both temperature and glass composition. As described here, one can deal with them comprehensively by associating classical theories for ionic transport in ionic crystals and molten salts (sensitivity to temperature) and weak electrolyte solutions (sensitivity to composition). Despite several thousand papers published on the subject, however, the mixed alkali effect (Chapter 4.6) remains a permanent challenge and a test of the validity of all thermodynamic or microscopic approaches.

In the last 20 years, fast ionic conductive glasses have been synthesized, especially with Li^+ or Ag^+ cations. Their room-temperature conductivity reaches values close to that of usual electrolyte solutions, i.e. 10^{-3} – 10^{-4} S cm $^{-1}$, offering a promising potential for new applications as active components in thin film solid-state batteries (Chapter 9.5), electronic memories, or stamping processes.

Interest in electronic conductive glasses has been boosted by successful applications of their switching properties in electronic devices or their photoconductive properties. A particularity of most electronic-conductive oxide glasses is that they may simultaneously present ionic and electronic conductivities. Thus, they may include foreign atoms electrochemically into their vitreous structure by simultaneous electronic and ionic injections. This possibility will in particular lead to further advances in electrochromic devices (smart windows), glass electrodes associated with a glassy electrolyte in solid-state batteries, and programmable metallization cell memories.

In its p and n types, amorphous silicon probably exemplifies best the practical importance of electronic

conduction. To form these semiconductors, the first step is to eliminate the dangling bonds and their associated localized states in the band gap by glow discharge decomposition of silane, SiH_4 , on amorphous silicon through the formation of $\text{Si}-\text{H}$ bonds whose bonding states lie deep within the valence band. Mixing some fraction of gaseous PH_3 or B_2H_6 with the silane then produces either n- or p-type conductive amorphous silicon. The donor (P) or acceptor (B) states are located close to the conduction or valence bands, allowing for electronic conduction in these bands (extended states). These amorphous semiconductors are now used in the design of solar cells whose lower cost compensates for lower yields.

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4.3

Diffusion in Oxide Glass-forming Systems

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1 Introduction

When oxide glasses are synthesized from a heterogeneous mixture of starting products, homogenization of the chemical composition during the melting process is ultimately achieved through diffusion (Chapter 1.3). Likewise, the chemical and physical durability of glasses is often controlled by diffusion kinetics [1]. Diffusivity, the property characterizing the timescale of diffusion, is in addition an indispensable parameter for understanding magmatic processes, such as magma mixing and the growth of crystals and bubbles from silicate melts. Beyond practical applications, the variations of diffusivity with either the nature of atomic species or with changing physicochemical parameters provide important insight into the structure of oxide glasses and melts. Diffusion is also intimately associated with other transport processes, such as viscous flow and electrical conduction.

These various features will form the backdrop of this chapter where we will first describe diffusion in physical and chemical terms and continue with a summary of the experimental methods used to measure diffusivities. The influence of species properties, composition (X), temperature (T), and pressure (P) on diffusivity will then be systematically examined. We end with a discussion of the investigation of diffusion with atomistic simulations and a consideration of possible future developments.

2 Physical and Chemical Description of Diffusion

2.1 Fick's Laws

Diffusion, an important means of mass transport, reflects thermally activated random walks of atomic species. The rate of diffusion is described by *diffusivity* or *diffusion coefficient* (denoted as D) with an SI unit of m^2/s . Because oxide gases and melts are isotropic systems, diffusivity is a scalar and is uniform in all directions. From a phenomenological perspective, a concentration gradient of a given component (∇C) will result in a net flux of that component as

$$\mathbf{J} = -D\nabla C, \quad (1)$$

known as Fick's first law of diffusion. Rigorously speaking, $\mathbf{J}$ arises from a chemical potential gradient ($\nabla\mu$), which is termed the thermodynamic driving force for diffusion. Diffusion acts to erase any heterogeneity across the system and leads to entropy production, as was elegantly treated by Onsager [2] in the framework of nonequilibrium thermodynamics. Readers are referred to [3] for a concise summary of the thermodynamic basis of the diffusion process. For diffusion in a non-steady-state system constrained by mass conservation, the concentration at a point space changes with time (t) as the divergence of $\mathbf{J}$,

$$\partial C / \partial t = \nabla \cdot (D\nabla C), \quad (2)$$

which is known as Fick's second law of diffusion. Analytical solutions of Eq. (2) for various initial and boundary conditions are available in [4].

2.2 Diffusion Mechanisms

From an atomistic perspective, diffusion can occur through a variety of mechanisms. At temperatures below the glass transition, a glass is essentially a solid with an

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amorphous network structure hereafter referred to as the *matrix*. Hence, the diffusion mechanisms operating in glasses are similar to those found in crystalline solids, albeit with a larger variety of structural sites.

A small neutral atom such as He can jump from one interstitial site to another through a bottleneck or energetic saddle point, interacting negligibly with the matrix. This process is referred to as the *direct interstitial mechanism*. When the atom (or ion) in question is of similar size as matrix atoms, two neighboring atoms may exchange their positions. However, this *direct exchange* mechanism is energetically very unfavorable. A rotational move of three or more atoms in concert entails less matrix distortions, but such a *ring mechanism* is rather complex. Another collective mechanism of diffusion is the *indirect interstitial* mechanism (or *interstitialcy mechanism*), with which an interstitial atom replaces a matrix atom, and the latter enters into an interstitial site. Still, the easiest pathway for diffusion is atom hopping into a vacant matrix site, referred to as the *vacancy mechanism* (see [1, 5] and Chapter 4.2 for more details about the mechanisms of ionic transport in oxide glasses).

In contrast to glasses, either stable or supercooled melts are intrinsically dynamic systems characterized by continuous occurrence of ionic transport, bond breaking and formation, and the interconversion of differently coordinated species. These interatomic rearrangements are collectively termed structural relaxation (Chapter 3.7). For small neutral species, the diffusion mechanism in a melt may not be fundamentally different from that in a glass (i.e. the interstitial mechanism). But for ions more closely contributing to structural relaxation (e.g. network-forming cations), diffusion may involve the formation of complex transition-state species, such as five-coordinated Si in the case of silicate melts. Upon cooling, relaxation time increases, and a melt is transformed into a glass at the glass transition temperature (T_g), where the relaxation time becomes longer than the timescale of the experiment (Chapter 3.7). That is, structural relaxation essentially stops.

2.3 Diffusion Distance

By considering the collective motion of Brownian particles, Einstein [6] derived that the diffusivity of an atomic species is related to its mean-square displacement $|\mathbf{R}(t) - \mathbf{R}(0)|^2$ by

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle}{6t}. \quad (3a)$$

Alternatively, diffusivity may be described as

$$D = \frac{L^2 \nu}{6} f, \quad (3b)$$

where L is the jump distance, ν is the jump frequency, and $f (\leq 1)$ is the correlation factor that is introduced because the jump probability may depend in part on the preceding jump. As an example, f approaches unity in the case of a tiny amount of a diffusing species hopping by the interstitial mechanism. From Eq. (3a), the diffusion distance in a given direction (x) can be estimated with

$$\Delta x \approx \sqrt{2Dt}. \quad (4)$$

Both Eqs. (3a) and (4) are referred to as the Einstein–Smoluchowski equation. Of particular practical interest is the fact that any process obeying Eq. (4) may be assumed to be diffusion controlled. This is, for example, the case of the kinetics of redox reactions (Chapter 5.6).

2.4 Types of Diffusion

In describing a diffusion process, the reference frame used is of key importance. This is why theoretical simulations invariably involve a fixed origin with respect to which all coordinates are described. Likewise, a reference point or plane on the material is also required in experimental studies. As driven by gradients in chemical potential, diffusion in a multicomponent glass-forming system must in addition be referred to some elements of the matrix: diffusion of a specific component is called *self-* or *cross-diffusion* depending on whether it is referred to itself or to other components. In atomistic simulations, individual atoms can be distinguished, so self-diffusivity is straightforward to derive with Eq. (3a).

Experimentally, however, individual atoms cannot be tracked so that the trick used to investigate self-diffusion is to introduce a distinct isotope, often radioactive, of the same element (whose mass difference may introduce some bias). In practice, the most common case of self-diffusion is that of *tracer diffusion* when ppm amounts or less of an isotopic tracer are introduced so as to produce only negligible concentration gradients [3, 7].

Diffusion in a system of three or more distinct chemical species is referred to as *multicomponent diffusion*, the special case of two species being known as *binary diffusion*. Owing to cross-diffusion in multicomponent systems, *uphill diffusion* (aligned $\mathbf{J}$ and ∇C) may occur, representing an apparently negative diffusivity that gives rise to an increase of the gradient of chemical composition (but not in chemical potentials). Finally, diffusion may be complicated by a chemical reaction, such as the interconversion between H_2O and OH in the case of H diffusion. This situation is referred to as *multispecies diffusion* [7]. These complexities notwithstanding, our

discussion will focus mostly on the self-diffusivity or tracer diffusivity of individual components or species.

3 Experimental Methods for Determining Diffusivity

The diffusivity of atomic species at fixed temperature (T) and pressure (P) in oxide glasses and melts can be determined by direct or indirect methods. The former are based on Fick's law of diffusion. Appropriate analytical techniques are applied to measure a diffusion profile or a bulk exchange produced by a thin source, a diffusion couple, or other methods [4, 5, 8]. For volatile components, membrane permeation, sorption, and desorption methods are frequently used [9].

Indirect methods investigate other physical phenomena related to diffusion. If electrical conduction in an oxide glass or melt is dominated by the transport of a single ion (such as Na^+), the diffusivity of that ion may be derived from the measured electrical conductivity (σ) via the Nernst–Einstein equation:

$$D = H_R \frac{k_B T \sigma}{N q^2} = H_R D_\sigma, \quad (5)$$

where k_B is the Boltzmann constant, N and q are the number density (in m^{-3}) and charge (in C) of the ion, respectively, and H_R is the Haven ratio determined by the diffusion mechanism and the correlation factor (Chapter 4.2). The *conductivity diffusion coefficient* D_σ is usually greater than the self-diffusivity D (hence $H_R \leq 1$). Another electrical method is square-wave voltammetry, which can be used to quantify the diffusivity of heterovalent elements in low-viscosity melts (Chapter 5.9).

Several compilations of diffusivity data in oxide glasses and melts are available [9–12]. For convenience, selected data sets are presented in Tables 1 and 2 for silicate and nonsilicate systems, respectively. The following three sections will elaborate on the variation of diffusivity with the intrinsic properties of diffusing species and the basic extrinsic parameters composition, temperature, and pressure. For a glass, thermal history (which governs T_g) may also have a detectable effect on diffusivity. Indeed, the dependence of properties on thermal history is an obvious indicator that a glass is not in internal thermodynamic equilibrium (Chapter 3.2).

4 Influence on Diffusivity of Species Properties

As illustrated in Figure 1 by comparisons between silica and albite ($\text{NaAlSi}_3\text{O}_8$) glasses and melts, atomic species show distinct diffusivities under similar T , P conditions.

The role played by the mass of the diffusing species is insignificant. By contrast, valence and size are two determining factors of diffusivity. Because of weaker interactions with the matrix, species with a small size and low electrical charge requires less energy to diffuse. Not surprisingly, neutral molecules and alkalis thus have higher diffusivities than other groups of elements (Figure 1). For species with valence $Z = 0$ or ± 1 , diffusivity always decreases with species size within each group (e.g. noble gases, alkalis, and halogens). However, this trend no longer holds for ionic species with $|Z| > 1$ (such as alkaline earths in Figure 1b); instead, diffusivity may increase with ionic radius (r). This effect probably results from decreasing field strength (Z^2/r), as r increases, which induces a weaker impeding response from the surrounding charge density.

Broadly speaking, volatile species diffuse faster than network-modifying cations, which in turn diffuse more rapidly than network-forming cations (such as Si^{4+} in silicate systems). The diffusivity of volatile species and low-field-strength network modifiers (such as Na^+) depends more favorably on their intrinsic properties and may therefore be referred to as *intrinsic diffusivity* [13]. That is, these species move largely on their own. By contrast, the diffusivity of network formers be referred to as *extrinsic diffusivity* because it is intimately associated with the matrix structure and is therefore more sensitive to extrinsic parameters (X , P , T), which primarily affect the network structure. Below the glass transition, network formers are essentially immobile. At high temperature, the extrinsic diffusivity may approach the *viscosity diffusion coefficient* D_η calculated with the Stokes–Einstein relation,

$$D_\eta = (k_B T) / (6\eta\pi r), \quad (6a)$$

where η is viscosity, from the assumption that diffusion and viscosity involve the same structural entities. For silicate and possibly other oxide glass-forming systems, however, the Eyring relation based on the transition-state theory [14] is more appropriate,

$$D_{\text{Eyr}} = (k_B T) / (\eta L), \quad (6b)$$

where D_{Eyr} is the *Eyring diffusivity* and L is the jump distance often taken as 2.8 Å, the diameter of the O^{2-} ion. A close match often exists between D_{Eyr} and the extrinsic diffusivity as represented by Si and O diffusivities in silicate melts, except when O diffuses by a shortcut mechanism, such as transport by H_2O or O_2 (Figure 1).

The diffusivity differences between various species shrink with increasing temperature and pressure and depend to some extent on composition. At least for silicates at $T < 2000$ K and $P < 2$ GPa (Table 1; Figure 1),

Table 1 Arrhenius parameters for diffusion in silicate glasses and melts.

Composition	Species	T range (K)	P (MPa)	D_0 (m ² /s)	H_a (kJ/mol)	References ^a
Silica (SiO ₂)						
Fused quartz	He	573–1307	≤0.1	7.4×10^{-8}	27.7	B10
Fused quartz	Ne	273–1257	≤0.1	1.0×10^{-8}	41.0	B10
Herasil 1	Ar	873–1373	≤0.1	2.4×10^{-10}	96.0	B10
Infrasil & Suprasil	CO ₂	1068–1368	200	3.8×10^{-9}	118	B10
Herasil 1	Kr	973–1573	≤0.1	2.2×10^{-9}	154	B10
Herasil 1	Xe	1273–1873	≤0.1	6.3×10^{-6}	293	B10
Infrasil	Na	523–846	0.1	4.0×10^{-5}	108	J99
Infrasil	Na	846–1273	0.1	3.4×10^{-6}	88.3	J99
Amersil & Suprasil	K	1073–1273	0.1	8.0×10^{-8}	126	J99
Amersil & Suprasil	Rb	773–1273	0.1	4.6×10^{-9}	150	J99
Amersil & Suprasil	Cs	903–1273	0.1	1.7×10^{-8}	212	J99
KSG	Ca	1073–1473	0.1	4.2×10^{-7}	234	J99
KSG	Ba	1273–1473	0.1	1.4×10^{-4}	307	J99
KSG	Zn	1073–1473	0.1	1.6×10^{-8}	187	J99
KSG	Cd	1073–1473	0.1	1.1×10^{-7}	216	J99
Puropsil A	Si	1383–1683	0.1	3.3×10^{-2}	579	J99
Amersil	O	1123–1523	≤0.1	2.0×10^{-13}	121	J99
Albite (NaAlSi ₃ O ₈)						
Albite	He	298–673	≤0.1	5.0×10^{-8}	67.0	B10
Albite	Ne	473–773	≤0.1	2.2×10^{-6}	95.0	B10
Albite	Ar	673–1273	≤0.1	9.0×10^{-8}	133	B10
Albite	Kr	873–1373	≤0.1	4.3×10^{-7}	168	B10
Albite	Xe	1173–1323	≤0.1	2.9	357	B10
Albite	Li	742–1183	0.1	5.9×10^{-6}	88.2	Z10
Albite	Na	623–1068	0.1	3.0×10^{-8}	49.1	Z10
Albite	K	610–1262	0.1	2.0×10^{-7}	100	Z10
Albite	Rb	793–1268	0.1	3.0×10^{-7}	132	Z10
Albite	Cs	978–1313	0.1	1.5×10^{-2}	284	Z10
Albite	Mg	1073–1293	0.1	1.8×10^{-5}	234	Z10
Albite	Ca	923–1298	0.1	3.5×10^{-6}	159	Z10
Albite	Sr	918–1293	0.1	3.6×10^{-6}	160	Z10
Albite	Ba	1073–1293	0.1	6.0×10^{-6}	188	Z10
Albite	Si	1438–1831	0.1	1.4×10^{-4}	337	Z10
Albite	Ga	1427–1775	0.1	3.6×10^{-1}	425	Z10
Albite	F	1473–1673	0.1	1.8×10^{-9}	121	Z10
Soda-lime systems						
72.2SiO ₂ ·11.9CaO·15.9Na ₂ O	Na	473–823	0.1	7.6×10^{-7}	92.1	J99
74SiO ₂ ·12CaO·14Na ₂ O	K	620–838	0.1	1.3×10^{-6}	126	J99
71.7SiO ₂ ·12.8CaO·15.5Na ₂ O	Rb	723–808	0.1	4.0×10^{-11}	86.7	J99
71.7SiO ₂ ·12.8CaO·15.5Na ₂ O	Cs	723–808	0.1	3.0×10^{-12}	86.7	J99
74SiO ₂ ·10.7CaO·15.3Na ₂ O	Ca	747–818	0.1	4.0×10^{-3}	225	J99
71.7SiO ₂ ·12.8CaO·15.5Na ₂ O	Sr	723–808	0.1	9.0×10^{-7}	164	J99

Table 1 (Continued)

Composition	Species	<i>T</i> range (K)	<i>P</i> (MPa)	<i>D</i> ₀ (m ² /s)	<i>H</i> _a (kJ/mol)	References ^a
71.7SiO ₂ ·12.8CaO·15.5Na ₂ O	O	733–798	0.1	2.0×10^{-1}	278	J99
83.7SiO ₂ ·16.3Na ₂ O	Na	473–723	0.1	2.8×10^{-6}	89.2	J99
Natural systems						
Rhyolite	Na	411–1173	≤200	1.3×10^{-6}	84.9	Z10
Rhyolite	Si	1573–1773	1000	1.0×10^{-10}	139	Z10
Rhyolite (3.5 wt % H ₂ O)	Na	973–1173	210	3.3×10^{-7}	68.2	Z10
Rhyolite (3.5 wt % H ₂ O)	Si	1373–1473	1000	2.6×10^{-8}	128	Z10
Dacite	Na	1574–1675	0.1	6.5×10^{-5}	152	Z10
Dacite	Si	1573–1773	1000	5.6×10^{-2}	383	Z10
Andesite	Na	1551–1675	0.1	9.3×10^{-7}	100	Z10
Andesite	Si	1488–1673	550	6.2×10^{-2}	315	Z10
Basalt	Na	1577–1673	0.1	9.6×10^{-5}	163	Z10
Basalt	Si	1593–1873	1000	3.7×10^{-6}	170	Z10

^a B10 = Behrens [9]; J99 = Jain and Hsieh [10]; Z10 = Zhang et al. [12]. Some Arrhenius parameters obtained from new fits to the original experimental data.

Table 2 Arrhenius parameters for diffusion in nonsilicate glasses and melts.

Composition	Species	<i>T</i> range (K)	<i>P</i> (MPa)	<i>D</i> ₀ (m ² /s)	<i>H</i> _a (kJ/mol)	References ^a
Borate						
B ₂ O ₃	He	326–409	≤0.1	$1.5 \times 10^{-10} T$	19.4	J99
96.4B ₂ O ₃ ·3.6Na ₂ O	He	370–408	≤0.1	$6.0 \times 10^{-11} T$	21.1	J99
92.7B ₂ O ₃ ·7.3Na ₂ O	He	392–441	≤0.1	$4.8 \times 10^{-11} T$	24.7	J99
88B ₂ O ₃ ·12Na ₂ O	Na	523–593	0.1	1.3×10^{-7}	123	J99
84B ₂ O ₃ ·16Na ₂ O	Na	573–633	0.1	7.0×10^{-8}	108	J99
76B ₂ O ₃ ·24Na ₂ O	Na	543–683	0.1	3.1×10^{-8}	82.5	J99
84B ₂ O ₃ ·16Na ₂ O	Ag	523–593	0.1	2.4×10^{-7}	113	J99
Germanate						
GeO ₂	He	403–493	≤0.1	$8.0 \times 10^{-11} T$	29.1	J99
GeO ₂	Na	573–673	0.1	4.0×10^{-6}	99.0	J99
98GeO ₂ ·2Na ₂ O	Na	473–583	0.1	1.3×10^{-6}	103	J99
92.5GeO ₂ ·7.5Na ₂ O	Na	473–583	0.1	1.8×10^{-7}	101	J99
91.2GeO ₂ ·8.8Na ₂ O	Na	473–583	0.1	2.5×10^{-7}	103	J99
84.4GeO ₂ ·15.6Na ₂ O	Na	473–583	0.1	6.3×10^{-8}	89.2	J99
Phosphate						
50P ₂ O ₅ ·50Na ₂ O	Na	453–528	0.1	9.7×10^{-7}	74.9	J99
47.6P ₂ O ₅ ·47.6Na ₂ O·4.8Al ₂ O ₃	Na	443–593	0.1	3.0×10^{-6}	78.5	Z03
43.5P ₂ O ₅ ·43.5Na ₂ O·13Al ₂ O ₃	Na	443–593	0.1	1.2×10^{-6}	74.0	Z03
37P ₂ O ₅ ·37Na ₂ O·26Al ₂ O ₃	Na	443–593	0.1	1.4×10^{-7}	66.1	Z03

^a J99 = Jain and Hsieh [10]; Z03 = Zhabrev and Sviridov [11].

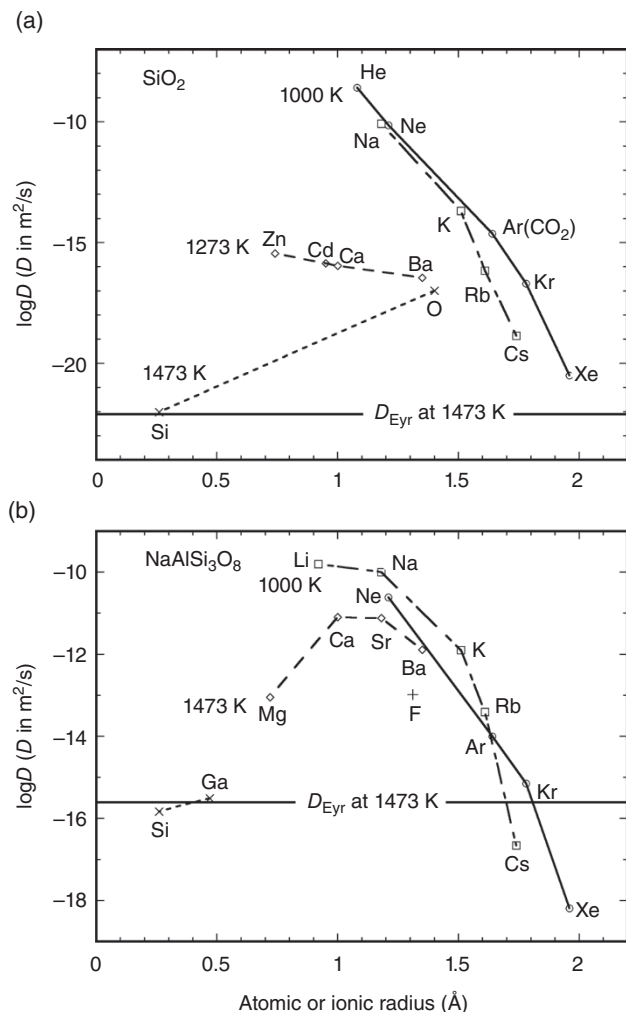


Figure 1 Contrasts between the effects of size and electrical charge on atomic diffusivities in glasses and melts of silica (a) and albite (b) [9, 12]. Atomic or ionic radii for a coordination number of 4 for Si, Ga, and F; 6 for noble gases, divalent cations, and O; and 8 for alkalis. Eyring diffusivities included as a horizontal line for comparison. The faster diffusion of O than Si in silica melt may be due to a shortcut mechanism.

however, chemical species can be roughly lined up in a diffusivity sequence:

$$\begin{aligned} \text{Si} < \text{REE} < \text{Mg} < \text{Xe} < \text{Cs} < \text{Ba} \approx \text{Kr} \approx \text{Sr} \approx \\ \text{Ca} < \text{Rb} \approx \text{Ar} \approx \text{CO}_2 < \text{K} < \text{Ne} \approx \text{Na} \approx \text{Li} < \text{He}, \end{aligned} \quad (7)$$

where REE indicates the rare earth elements.

5 Compositional Control

Chemical composition determines the structure of a glass-forming system and sets up the matrix environment for diffusion. But the compositional control on diffusivity

is complicated and difficult to model, to say the least. As implied by Eqs. (6a and 6b), diffusivity, for example, generally decreases with increasing viscosity which, other things being equal, generally means an increasing degree of polymerization or increasing concentration of network formers. Rather robust as is this rule, there are still a number of exceptions to it.

5.1 Silicate Systems

Silicates are the most comprehensively studied among all kinds of oxide glass-forming systems. In this case, the concentration of SiO_2 may be conveniently used as a first-order index of polymerization. Assuming Si, Al, and ferric iron to be network formers, one measures more accurately (de)polymerization as the number of non-bridging oxygen atoms per tetrahedrally coordinated cation as $\text{NBO}/T = [2 \text{ O}/(\text{Si} + \text{Al} + \text{Fe}^{3+}) - 4]$ [15]. From basalt to andesite to dacite to rhyolite compositions (Figure 2), the diffusivity of Si among most other ions decreases rapidly along the sequence of decreasing NBO/T for natural calc-alkaline melts, in agreement with the trend predicted by Eqs. (6a and 6b). However, there appears to be a slight concomitant increase in Na diffusivity (Figure 2). One possible explanation for this special phenomenon is that rhyolitic melt has a higher “ionic porosity” or “free volume,” the fraction of melt volume not occupied by ions, than basaltic melt [13].

Volatiles, and water in particular, have a tremendous effect on diffusivity in silicate systems. Adding H_2O promotes the diffusion of all species as it disrupts the network structure through the reaction $\text{H}_2\text{O} + \text{SiOSi} = 2 \text{ SiOH}$, with an associated drop in viscosity. The enhancing

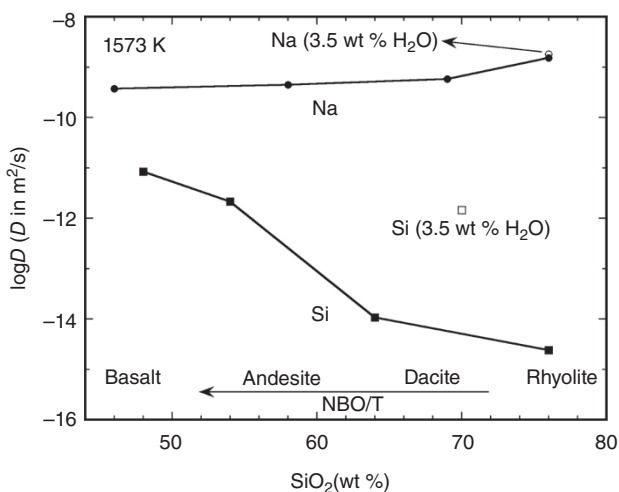


Figure 2 Na and Si diffusivities in natural silicate melts with different degrees of polymerization [12]. Water has a more pronounced influence on Si diffusivity than on Na diffusivity.

role of water on diffusivity is especially strong for ions with high field strength, such as Si^{4+} (Figure 2).

5.2 Nonsilicate Systems

Diffusivity data for nonsilicate systems are limited. In borate glasses $x \text{ Na}_2\text{O} \cdot (100 - x) \text{ B}_2\text{O}_3$, He diffusivity decreases with x increasing from 0 to 7.3, whereas Na diffusivity increases with x increasing from 12 to 24 (Figure 3a). As Na_2O is added to vitreous B_2O_3 , progressively more trigonal boron converts to tetrahedral configuration, which entails the *boron anomaly* and ensures the chemical stabilization of borate glass (Chapter 7.6). Only after x reaches ~ 25 , does borate glass start being depolymerized by further Na_2O incorporation [5]. The combined He and Na diffusivity data appear to be

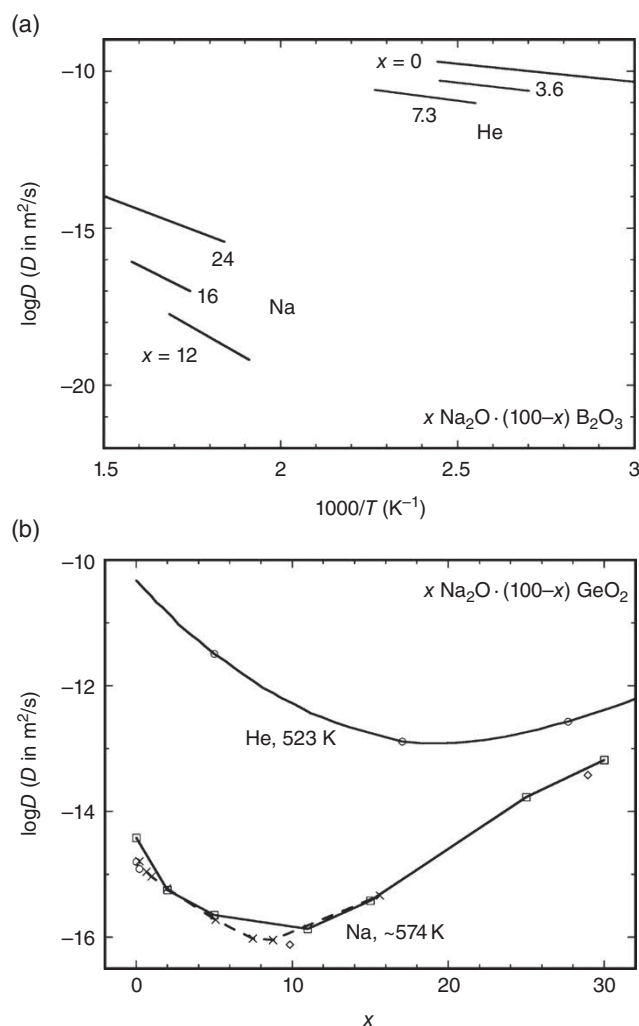


Figure 3 Differing effects of network-former coordination changes on He and Na diffusivities in alkali borate (a) and alkali germanate (b) glasses [10].

qualitatively consistent with this structural analysis, except that the diffusivity minimum, at least for Na, is expected to be at $x < 10$ instead of at $x = 25$.

Diffusivity minima have been unambiguously observed in germanate glasses $x \text{ Na}_2\text{O} \cdot (100 - x) \text{ GeO}_2$, at $x \approx 19$ for He and $x \approx 9$ for Na (Figure 3b). As found for borate glasses, the observed trend for germanate glasses is associated with a coordination change of the network former, in this case the transformation of tetrahedral Ge to octahedral Ge, until the appearance of non-bridging oxygen at $x \approx 18$. Loose bonding between Na^+ and $[\text{GeO}_{6/2}]^{2-}$ or $[\text{BO}_{4/2}]^-$ group may account for the early increase of Na diffusivity [1].

By comparing Na diffusivity in various types of binary glasses with similar mole fraction of Na_2O (~ 0.16 , except for the phosphate), one finds that Na diffusion becomes slower from phosphate to silicate to germanate and to borate glass (Figure 4). While this trend may not be absolutely transferrable to the diffusivity of other species, it does appear to be consistent with the fact that the proportion of non-bridging oxygen decreases along this sequence.

5.3 Mixed Alkali Effect

A special phenomenon manifesting the complexity of compositional control is the so-called mixed alkali effect. Take a series of 20 $[x \text{ Na}_2\text{O} \cdot (1 - x) \text{ Rb}_2\text{O}] \cdot 80 \text{ B}_2\text{O}_3$ glasses as an example (Figure 5): as x increases from 0 to 1 (i.e. Rb is progressively replaced by Na), the Rb diffusivity monotonically decreases; likewise, a slowdown of Na diffusion occurs with decreasing x . At the end-member composition 20 $\text{Rb}_2\text{O} \cdot 80 \text{ B}_2\text{O}_3$, the Na diffusivity even drops below

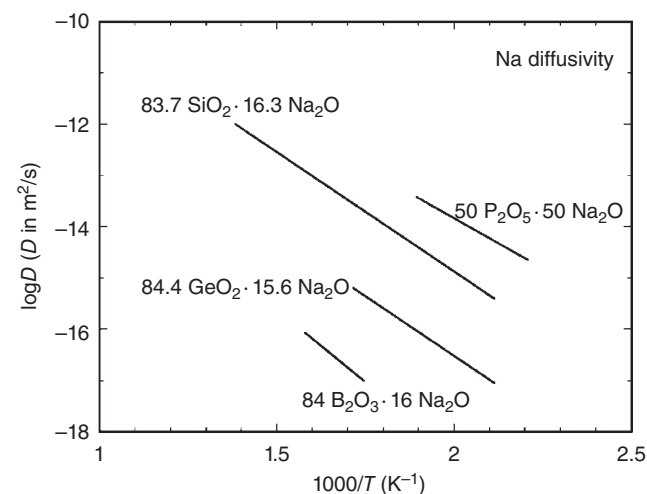


Figure 4 Influence of the glass matrix on Na diffusivity in various types of binary glasses with similar mole fraction of Na_2O (except for the phosphate) [10].

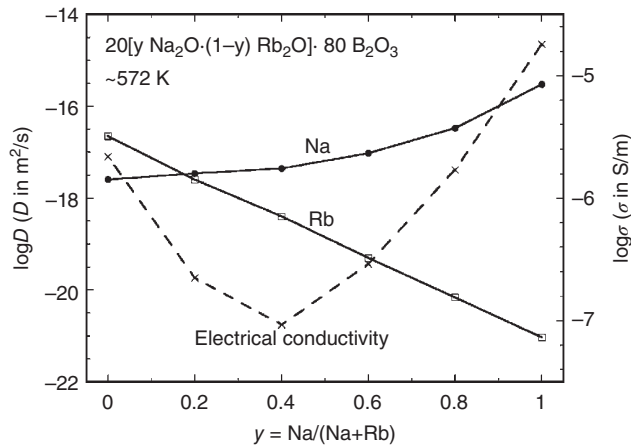


Figure 5 The mixed alkali effect as indicated by the variation of Na and Rb diffusivities and electrical conductivity in alkali borate glasses [5].

that of Rb, overturning the normal sequence of Eq. (7). Therefore, each alkali seems to impede the diffusion of the other alkali, resulting in a marked minimum in the electrical conductivity of glass (Figure 5). The mixed alkali effect is more pronounced with increasing size mismatch of the two alkalis and is common in all types of oxide glasses. However, there is still no consensus on its physical origin, with the electrodynamic interaction models, the hydrostatic stress models, and the defect models as the favored candidate mechanisms [1, 5, 16].

6 Temperature and Pressure Effects

6.1 Temperature Effects

For a given composition and a given species, diffusivity always increases with temperature and usually decreases with pressure, although there are fascinating exceptions in glass-forming systems that have provided significant insight into the mechanisms of diffusion. The “normal” behavior is often well described by an Arrhenius relation, which follows from the mechanical description of diffusion in the framework of Boltzmann statistics [3],

$$D = D_0 \exp\left(-\frac{H_a}{RT}\right) = D_0 \exp\left(-\frac{E_a + P\Delta V_a}{RT}\right), \quad (8)$$

where D_0 is the pre-exponential factor, H_a and E_a are the activation enthalpy and activation energy, respectively, ΔV_a is the activation volume, and R is the gas constant. The Arrhenius parameters D_0 and H_a are summarized in Tables 1 and 2 for silicate and nonsilicate systems.

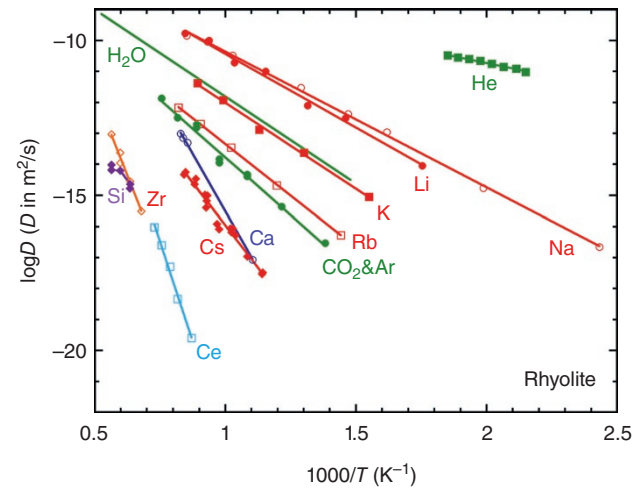


Figure 6 Convergence of diffusivities in a rhyolitic melt in the high-temperature limit [12].

For some volatiles, one describes diffusivities better by taking D_0 to be proportional to temperature [9].

In view of the thermally activated nature of the diffusion process, H_a and E_a are positive so that, as already noted, diffusivity always increases with temperature. For the diffusion of various species in a matrix of given composition, the sequences of E_a and diffusivities are generally opposite. The activation enthalpy can be as low as ~ 20 kJ/mol for He diffusion and as high as ~ 400 kJ/mol for Si diffusion (Tables 1 and 2). This negative correlation between E_a and D_0 is known as the compensation law and has the important consequence that diffusivities tend to converge in the high-temperature limit (Figure 6). With decreasing temperature, the diffusivities of atomic species decrease following divergent paths governed by E_a , which expresses the decoupling between atomic mobility and structural relaxation [15].

Below the glass transition range or above the liquidus, the linear relationship between the logarithm of diffusivity and $1/T$ implied by Eq. (8) is rather robust. Some experimental data even suggest a constant H_a across the glass transition. However, there is also evidence for a change of H_a between glass and melt, which has important implications for the common first-order view of glasses as effectively frozen-in liquid structures. For O and Na diffusion in a soda-lime silicate (i.e. a window glass), two linear segments of $\ln D$ versus $1/T$, with different slopes, are connected by a nonlinear curve in the intermediate temperature range (Figure 7). Intersection of the curve and the low-temperature segment produces an inflection point close to T_g , which is more easily recognizable for O than for Na. In other systems, the inflection point in the Na diffusivity curve can be lower than the calorimetric T_g by up to 100 K. The oxygen diffusivity

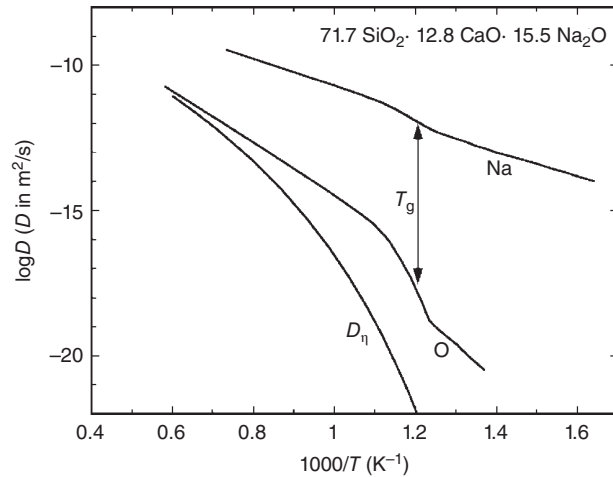


Figure 7 Effects of the glass transition (T_g) on the diffusivities of O and Na in a soda-lime silicate system, with the Eyring diffusivity shown for comparison [15].

approximates the Eyring diffusivity at high temperature, but their difference increases substantially down to T_g .

Cooling results in an increase in the relaxation time of the α -process (or the primary relaxation) which, as controlling viscous flow, is the major component of structural relaxation [17]. When plotted against $1/T$, the reciprocal of relaxation time has a shape similar to the Eyring diffusivity curve in Figure 7. In oxide glasses below T_g , the Arrhenius nature of diffusivity indicates that diffusion belongs to the category of β -processes (or secondary relaxations), which are associated with shorter timescales and less structural modification than the α -process [17]. In oxide melts, the combination of the α - and β -processes may explain the complex temperature dependence of diffusivity in the intermediate temperature range above T_g (Figure 7). With increasing temperature, the α -process will eventually take over control of diffusion, sooner for network formers and oxygen than for network modifiers.

6.2 Pressure Effects

In glass science, the pressure dependence is not of major concern to diffusion. Limited studies [18] have yielded activation volumes of $6\text{--}33 \times 10^{-6} \text{ m}^3/\text{mol}$ at $P < 1 \text{ GPa}$ for Na and Rb diffusion in alkali borate glasses (Figure 8a).

In earth and planetary sciences, diffusion in silicate melts under high pressure has in contrast been investigated extensively for application to geological processes at great depths. The effects of pressure on the diffusion of most species (such as for Ar, Figure 8b) are negative, which can be understood in light of the “free volume” concept. In polymerized melts, however, Si and

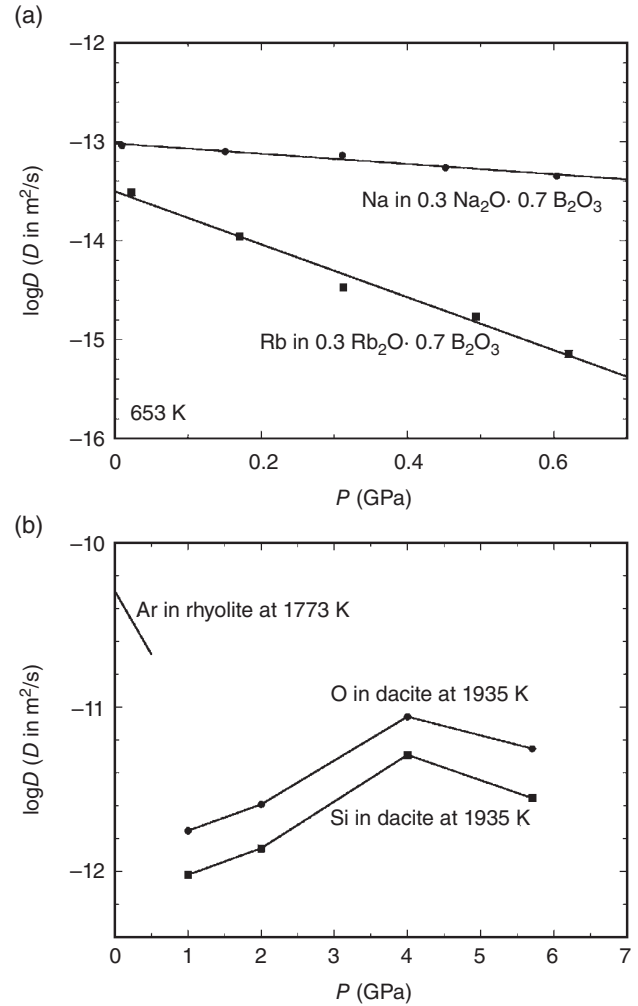


Figure 8 Pressure effect on diffusivity in alkali borate glasses (a) and natural silicate melts (b) [9, 18].

O diffusivities first increase with pressure (corresponding to negative ΔV_a), before the trend reverses at several GPa (Figure 8b). Consistent with Eq. (6b), the positive pressure influence on Si and O diffusivities is often accompanied by a decrease of melt viscosity. These effects are associated with pressure-induced changes in melt structure, which however act little on the diffusion of network modifiers and volatiles.

7 Insights from Molecular Dynamics Simulations

Thanks to the advances in computation technology, molecular dynamics (MD) simulations can now be readily used to investigate diffusion in oxide melts at high T and P that are difficult to achieve experimentally. In addition to their practical interest, they provide an intrinsically

atomistic perspective. The computationally expensive first-principles molecular dynamics (FPMD) is afflicted by limits on simulation size and time, but theoretically delivers more accurate results than classical MD. A detailed treatment of computational studies of diffusion is given in [3] and Chapter 2.9.

Although discrepancies between experimental and computational diffusivities occur, computations show their true power in elucidating the underlying structural rationale and relative trends of D versus X , P , T . For example, the increase of Si and O diffusivities with pressure in polymerized silicate melts was predicted by MD simulations [19] before it was experimentally confirmed. MD simulations further indicate that this phenomenon is associated with pressure-induced changes in the lifetimes of Si coordination species.

Owing to the short timescales involved, MD is only viable for high-temperature investigations, i.e. for liquid systems. Other techniques for characterizing diffusion in solids are available, but are usually only applied to crystalline materials. In addition, the currently accessible system sizes of MD simulations pose limits to inquiry as the glass transition is approached, as locally heterogeneous dynamics with slow and fast diffusing regions may lead to non-ergodic behavior, and long-range interactions are likely to play an important role.

8 Perspectives

An enormous amount of diffusivity data in oxide glass-forming systems has been collected in the past century with a variety of experimental methods. From a phenomenological point of view, we have attained substantial appreciation on how diffusivity varies with species properties, composition, temperature, and pressure. However, the physical rationale behind the observed trends is not totally clear yet. The mixed alkali effect and the temperature dependence of diffusivity in the vicinity of glass transition are just two examples of complex diffusion phenomena that need further investigation.

A complete account of the interactions between atoms may hold the key to understanding the mechanisms of diffusion and the trends of diffusivity. In essence, diffusion and structural relaxation in glass-forming systems are many-body problems, which unfortunately remain unresolved in condensed matter physics and statistical mechanics [20]. In that regard, first-principles simulations, which make no a priori assumption of interatomic interactions, have the potential to bring major breakthroughs. On the basis of a deeper understanding of the physics of diffusion, along with the accumulation of

more reliable experimental and computational diffusivity data, it will then become possible to develop much needed multivariate diffusivity models, which will find plenty of applications in the development of new oxide glasses.

Acknowledgments

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4.4

Chemical Diffusion in Multicomponent Glass-forming Systems

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1 Introduction

Diffusive processes are of pivotal importance in the glass-making industry. Whereas advection, for instance, plays a major role in large-scale mixing of the molten batch, small-scale chemical heterogeneities are erased by diffusive transport (Chapters 1.1 and 1.2). In the opposite direction, diffusion-controlled processes also take place to create chemical heterogeneities when devitrification or, more generally, any phase separation is induced as done in the production of glass ceramics (Chapter 7.11). Finally, glass durability is at least partially controlled by the diffusivities of chemical species such as water within the glass network. Whether upon fabrication or use, chemical diffusion is thus a fundamental process particularly relevant to glass. It remains to be understood better, however, especially to optimize glass manufacturing in terms of the temperature and composition dependences of the characteristic time and length scales of diffusion processes.

As a matter of fact, different quantities and concepts are intermingled in the general term of *diffusion*. First, the diffusion of a given component is more precisely named *self diffusion* when an atomic random walk is studied in reference to the component itself (Chapter 4.3). Experimentally, the self-diffusivity can be determined by isotopic tracing or from diffusion profiles of the component of interest present in trace amounts such that concentration gradients are negligible. This situation reproduces the common picture of diffusion of the random walk of a tracer in a solvent. From atomistic simulations, the self-diffusion coefficient can also be calculated and then related to transport properties such as viscosity

and electrical conductivity (cf. Chapter 4.6). A third kind of diffusion coefficients is associated with much more common industrial and natural systems where chemical heterogeneities are characterized by large concentration differences for one or several components. This general situation of mass transport leading to a local change in composition is referred to as *chemical diffusion* or *interdiffusion*. It is the subject of this chapter.

Because the composition gradients of different components may interfere with one another, the interdiffusion rate of a given component may widely differ from the rate deduced from its self- or tracer-diffusion coefficient in similar melts. From macroscopic, phenomenological, or mathematical approaches, diffusive processes can be studied in a variety of ways. As generally based on Fick's equations, however, these provide little insight onto the microscopic processes at work in glasses and melts. In their simplest form, macroscopic descriptions can in addition yield apparently paradoxical quantities such as *negative* diffusion coefficients in multicomponent systems (i.e. diffusion acting against the chemical gradients of components).

Mechanistic approaches are, therefore, needed to arrive at a comprehensive picture merging the kinetic and thermochemical aspects of chemical diffusion. This chapter will thus begin with a review of this theoretical background. After a brief description of the experimental procedures to be followed in interdiffusion studies, diffusion in binary melts and relationships between self- and chemical diffusion will be presented. The general case of multicomponent systems will then be dealt with, particular attention being paid to uphill diffusion and diffusion paths. Finally, the composition and temperature dependences of diffusive coupling will be examined from the results obtained on ternary and quaternary aluminosilicate systems.

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2 Conceptual and Experimental Approaches

2.1 Fundamental Concepts

In 1855, the physician A. Fick (1829–1901) described diffusive mass transport by analogy with the celebrated heat equation published in 1822 by the mathematician J. Fourier (1768–1830). In isotropic media such as melts and glasses, Fick's first law thus relates the concentration gradient to diffusive flux of a component through

$$J = -D\nabla C, \quad (1)$$

where J , the diffusive density (analog of the heat flux), is negatively proportional to ∇C ; the local concentration gradient ($\sim$ temperature gradient), with a proportionality coefficient D defined as the *diffusion coefficient* ($\sim$ thermal conductivity), is expressed in the SI m^2/s unit. In the typical case where D is a positive scalar, a local change of the concentration of the element gives rise to a flux from the concentrated to the depleted part of the system. Equilibrium is then attained when concentrations ($\sim$ temperatures) are equal across the whole system.

If there are no sources or sinks for the component of interest and if convection is negligible, the concentration change of the component of interest in an elementary volume of the system is the difference between its incoming and outgoing fluxes. This mass conservation rule is referred to as Fick's second law and can be written for non-steady-state system as

$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C). \quad (2)$$

Analytical solutions of Eq. (2) have been given by Crank for a great many initial and boundary conditions [1]. Applications to multicomponent systems such as liquids and glasses of industrial and geological interest is not straightforward, however (cf. Chapter 4.3), because concentrations must sum to 1 (or 100%) at each point. In other words, any local decrease of the concentration of a component is compensated by increases of the concentrations of other components. In such systems, at least two gradients – and, therefore, two *fluxes* in opposite directions – are necessary to characterize the overall diffusive mass transport. How, then, can these fluxes be mutually related? The simple answer brought forward by Onsager [2] was to generalize Fick's equations with the assumption that the flux of component i is linearly related not only to its own concentration gradient but also to those of all other components:

$$J_i = -\sum_j (D_{ij} \cdot C_j), \quad (3)$$

where D_{ij} are the diffusion coefficients of component i along the concentration gradients of the other

components j . If one again assumes negligible convective transfer and the absence of sources or sinks for the component i , Fick's second law is expressed as

$$\frac{\partial}{\partial t} \begin{bmatrix} C_1 \\ \vdots \\ C_j \\ \vdots \\ C_n \end{bmatrix} = \begin{bmatrix} D_{11} & \cdots & D_{1j} \\ \vdots & \ddots & \vdots \\ D_{j1} & \cdots & D_{jj} \end{bmatrix} \cdot \frac{\partial^2}{\partial x^2} \begin{bmatrix} C_1 \\ \vdots \\ C_j \\ \vdots \\ C_n \end{bmatrix}, \quad (4)$$

where x is the relevant distance. When diffusion coefficients and concentrations are written in the form of two matrices, $\mathcal{D}$ and $\mathcal{C}$, respectively, Eq. (4) is expressed in a more compact manner as

$$\frac{\partial \mathcal{C}}{\partial t} = \mathcal{D} \cdot \frac{\partial^2 \mathcal{C}}{\partial x^2}. \quad (5)$$

Each of the coefficients of $\mathcal{D}$ characterizes the influence of a component j on the flux of component i . Because there are only $n - 1$ independent components, these coefficients constitute all together an $(n - 1) \times (n - 1)$ matrix where D_{ij} is not necessarily equal to D_{ji} . As for the n th component, it is often termed *dependent* because its concentration is determined from the others through mass conservation. For convenience, it is usually chosen among the slowest diffusing components. In oxide melts, network-forming cations (Si, Al, Ge, etc.) fit this definition since their diffusivity contrast with network-modifying cations considerably increases with decreasing temperatures.

2.2 Experimental Strategy

Any experimental approach has to be carefully designed to quantify diffusion timescales and chemical paths in a multicomponent system. Obviously, *tracer diffusion* experiments are of limited help because they do not reveal the complex coupling that may exist between the components of a system. Hence, it is necessary to investigate instead interdiffusion between two *end-member* melts whose overall compositions differ significantly, but not too widely; otherwise, Fick's formalism might not hold true any longer because of the dependence of diffusion coefficients upon bulk composition. In practice, gradients must be limited to a few wt % across the whole sample.

In addition, caution must of course be taken to use inert containers, to avoid devitrification upon reheating of the assemblage, to check the stability of the interface between the two end-members, and, in particular, to make sure that convective transport does not take place as it would dramatically change the timescale of melt homogenization. Therefore, at least a crude knowledge of the rheology and density of the two end-members is needed. To avoid convective transport, which is not always easy to

identify, a confining pressure on the assemblage may be applied with devices such as the piston-cylinder apparatus (e.g. [3]). Generally, however, it is more straightforward to put the densest glass at the bottom of the assemblage and to analyze the concentration of an added colored or isotopic tracer for ascertaining the lack of convection.

The number of experiments required to determine a diffusion matrix is also a key parameter that may temper the motivation of experimentalists. If the melt contains n components, then at least $n - 1$ independent concentration profiles must be measured [4]. Typically, the glasses juxtaposed to make the diffusion couple are selected symmetrically in compositional space relative to the target composition. Ideally, these diffusion profiles should not only intersect at the composition of interest but their eigenvectors should be colinear to in the eigenspace of the diffusion matrix [5]. The obvious difficulty in this respect is that these eigenvectors are generally unknown a priori. As a consequence, diffusion couples should be chosen, in the classical compositional frame, so that at least one component has a constant concentration. Finally, a conservative approach consists in making at least $2n$ experiments, with at least n independent diffusion couples and two different run durations in order to check the self-consistency of the data set [6].

3 Tracer vs. Chemical Diffusion

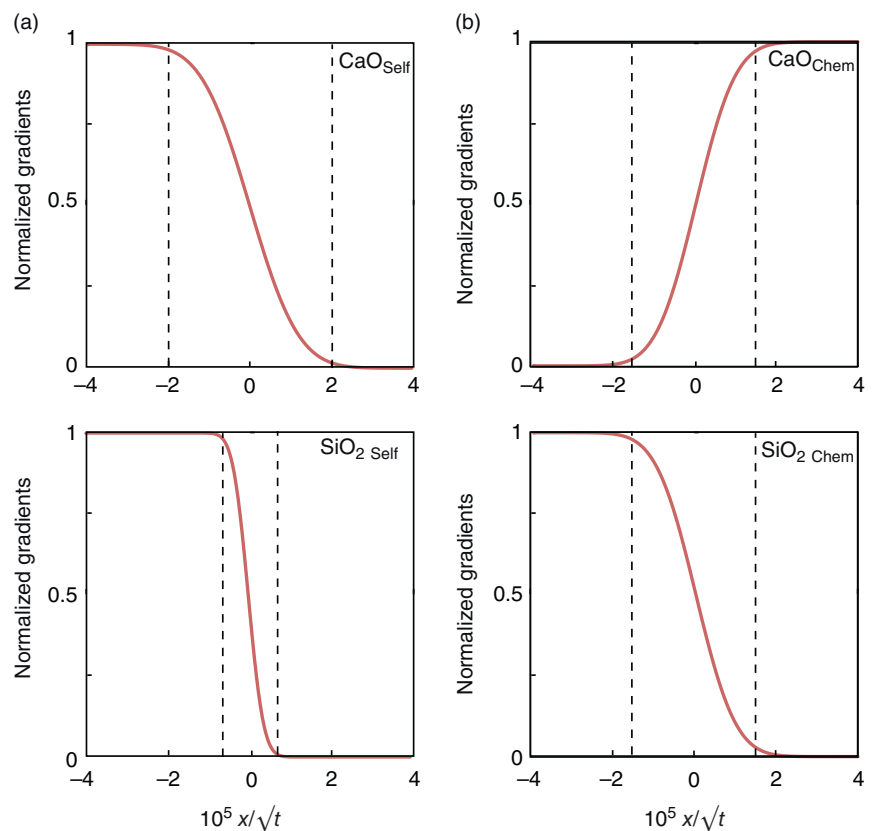
Extensive work by Liang et al. on the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system [3, 7–9] illustrates well the fundamental differences between self- and chemical diffusion (Figure 1). In the former, calcium moves almost 10 and 5 times faster than silicon and aluminum, respectively. At constant Al_2O_3 concentration, calcium diffuses in contrast more slowly and silicon faster than their respective isotopes in the absence of chemical-concentration gradients (Figure 1). In other words, the two fluxes have become strongly correlated.

This process has long been known for both molecular and ionic fluids. In binary molecular and metallic fluids in a fixed-volume frame, the mobility of atoms is strongly constrained by the fact that local volume changes are forbidden. This constraint of no net volume flux is accounted for by the formalism developed by Darken [10] for thermodynamically ideal systems:

$$D = X_2 D_1^* + X_1 D_2^*, \quad (6)$$

where D is the chemical diffusion coefficient, X_i is the mole fraction of component i , and D_i^* is its self-diffusion coefficient. For ionic (or electrolytic) fluids, electroneutrality must be conserved. Since local charge buildup is forbidden, Coulombic interactions are the main restoring

Figure 1 Differences in CaO and SiO_2 concentration profiles between self- (a) and interdiffusion (b) experiments on a calcium aluminosilicate melt [3, 7]. Normalized concentration profiles of CaO and SiO_2 produced during two distinct diffusion experiments. (a) Self-diffusion traced by isotopes, and (b) chemical diffusion of the two oxide components in a ternary melt (CAS). Experiments were performed on compositionally comparable melts at 1500°C . Source: Data from [3, 7].



force. The flux rates of diffusing species then couple under the condition of no net flux of electrical charges. For the interdiffusion of two cations (or anions) present in a binary solution, one can define in this case a mean diffusion coefficient representing a weighted mean of the self-diffusion coefficients. Buck [11], for instance, proposed the expression

$$D = \frac{D_1^* D_2^* (z_1^2 X_1 + z_2^2 X_2)}{z_1^2 X_1 D_1^* + z_2^2 X_2 D_2^*}, \quad (7)$$

where z_i is the electrical charge of ion i . As it should, Eq. (7) satisfies the limiting condition that, at infinite dilution of one of the two ions, its self- (or tracer-) diffusion controls the overall chemical diffusion in the solution. From Eqs. (6) and (7), it also follows that the long range of Coulombic forces causes the slower ion to impede the displacement of the faster one more effectively than forces due to volume changes. Other things being equal, interdiffusion would thus be slower for ions than for non-charged particles.

4 Diffusion in Multicomponent Systems

4.1 A First Approach: The Effective Binary Diffusion

In a multicomponent system, diffusive fluxes interfere in a similar though more complicated way because of the multiplicity of concentration gradients. Although the various components tend to diffuse at different rates according to their own self-diffusivity, the lack of both net volume flux and electrical charge buildup strongly constrains the overall diffusion timescale and path. To take care of this complexity, Cooper [12] introduced the simplest approach of *effective binary diffusion* whereby the multicomponent melt is treated as a pseudo-binary system in which the component of interest is taken as the *solute* and all other components are taken together as the *solvent*. The flux of the component of interest then takes the simple form given by Eq. (1) with an effective binary diffusion coefficient (EBDC) that integrates all coupling effects.

As a result, the EBDCs are in general not constant for a given diffusion couple and they also depend on the direction of diffusion in the composition space [13]. In CaO–Al₂O₃–SiO₂ melts [7], the measured EBDC of SiO₂ at constant viscosity is, for instance, almost 10 times lower for diffusion at constant CaO than at constant Al₂O₃ concentrations. Another important feature of effective binary diffusion is that they vary with time at a fixed position in a given diffusion couple [14]. Hence, the composition, time, and geometry dependences of

EBDCs further complicate applications of these parameters to systems different from those for which they have been determined. In general terms, EBDCs and D s are indeed different for a given component across a given diffusion couple. In spite of their complexity, their mutual relationships have been worked out [13] without making it possible, however, to account for the critical phenomenon of uphill diffusion. In summary, determinations of EBDCs do not help much to predict the general diffusion processes taking place in a multicomponent system. A more fundamental approach is needed.

4.2 The Fick–Onsager Thermodynamic Approach

In Onsager's [2] formulation of Fick's laws, equilibrium is attained when the concentrations of the n components are equal across the system, which correspond to the state of maximum entropy. But gradients in chemical potential, and not in concentrations, are the true driving force for diffusion since the whole process eventually leads to a minimum Gibbs free energy. Rather than in terms of observed compositional gradients, the flux of a given component i is, strictly speaking, better written as

$$J_i = -\sum_j L_{ij} \cdot \frac{\partial \mu_j}{\partial x}, \quad (8)$$

where μ_j is the chemical potential of component j and the L_{ij} are *Onsager's diffusion coefficients* forming the symmetric kinetic matrix $\mathcal{L}$. To relate these chemical potentials to the chemical compositions, which are actually measured, one simply can relate the $\mathcal{L}$ and $\mathcal{D}$ matrices with

$$\mathcal{D} = \mathcal{L}\mathcal{G}, \quad (9)$$

where $\mathcal{G}$ is another matrix that accounts for the thermodynamic mixing properties whose elements, G_{ij} , are given by

$$G_{ij} = \frac{\partial(\mu_i - \mu_n)}{\partial X}. \quad (10)$$

Referring to [8] for a summary of the mathematical properties of these matrices, we will limit ourselves here to mention briefly information on microscopic interactions between the melt components that can be drawn from this formalism when use is also made of models relating chemical diffusion to self-diffusion coefficients. In practice, $\mathcal{L}$ can be derived if $\mathcal{D}$ and $\mathcal{G}$ are known. With an extension of the Darken-type Eq. (6) and the Nernst–Planck-type Eq. (7) to multicomponent systems, Liang et al. [8], for instance, found that the diagonal terms of the $\mathcal{L}$ matrix represent the intrinsic mobility of each component whereas the off-diagonal terms contain

information on both volume relaxation and ionic interactions. The $\mathcal{G}$ matrix could itself be expressed as a product of $\mathcal{F}$ and $\mathcal{N}$ matrices, the former essentially reflecting the thermodynamic nonideality of the solution and the latter the partial molar volumes of the components. Modeling in this way their experimental data set for the ternary CaO–Al₂O₃–SiO₂ system [7], Liang et al. [8] demonstrated that kinetic interactions (volume relaxation and ionic interactions), partial molar volume changes, and thermodynamic nonideality all contributed significantly to the coupling between diffusing components so that none of these factors could be neglected.

4.3 Determination of the Diffusion Matrix

Once the set of $(n - 1)$ components defining the $(n - 1) \times (n - 1)$ diffusion matrix $\mathcal{D}$ has been selected, several techniques exist to obtain the coefficients of the diffusion matrix from a set of diffusion experiments between different end-members. Their common underlying principles are fits of theoretical predictions obtained with the sought-after diffusion matrix to experimental diffusion profiles (or other functions derived from them).

At a time when computational power was limited, the Boltzmann–Matano method [14] was favored in early interdiffusion studies. It was originally developed to investigate concentration-dependent diffusion in binary systems. It consists in first transforming Fick's law (a partial differential equation) into an ordinary differential equation through a Boltzmann transformation in terms of the rescaled variable $\xi = x/2\sqrt{t}$. The new form can then be solved numerically so that the coefficients of the diffusion matrix become the solutions of a linear system of such equations. Therefore, at least as many independent profiles as coefficients must be obtained to solve this linear system.

One advantage of the Boltzmann–Matano method is that a unique solution actually exists, which can be readily obtained from experimental concentration profiles. The method requires to compute the spatial integral of the concentration profiles, however, so that experimental errors accumulate and degrade the accuracy with which the diffusion matrix is computed. The standard χ^2 method relying on least-squares minimization of the differences between experimental and calculated profiles may alternatively be used.

For complex systems, minimizing the error is most conveniently done on the basis of the eigenvectors of the diffusion matrix, that is, along directions in the composition space that remain invariant in the course of the diffusion process. Let us define

$$\mathcal{D} = \mathcal{P}\mathcal{A}\mathcal{P}^{-1}, \quad (11)$$

where Λ is the diagonal matrix of eigenvalues λ_i and $\mathcal{P} = (\mathbf{v}_1, \dots, \mathbf{v}_{n-1})$ is the matrix of the eigenvectors $\mathbf{v}_i$. Each λ_i represents a diffusion coefficient associated with an eigenvector $\mathbf{v}_i$. The coefficients of $\mathbf{v}_i$ characterize the proportions of the species exchanged in the corresponding diffusion mechanism. Denoting by $\mathcal{C}$ the concentration vector on the basis of the eigenvectors (a linear combination of the concentrations of the different oxides), one obtains the equation

$$\frac{\partial \mathcal{C}}{\partial t} = \Lambda \cdot \frac{\partial^2 \tilde{\mathcal{C}}}{\partial x^2}. \quad (12)$$

Since Λ is a diagonal matrix, this expression represents a set of independent equations whose analytical solutions are similar to that obtained for the diffusion of a single species. They can thus be readily adjusted to the experimental profiles $\mathcal{C}$.

With a number $(n - 1)^2$ of coefficients to be determined, the complexity of the optimization process rapidly increases with n so that it is important to check that the true χ^2 minimum has been found. If so, the same solution must, for instance, be obtained with differing sets of starting parameters for the χ^2 minimization. To derive such starting values, one can use first the Boltzmann–Matano method or, more simply, select literature data. In any case, a successful initialization can be achieved from visual adjustments of literature data or of the new experimental results.

Because of measurement errors, it is of course recommended to overconstrain the optimization problem with more diffusion experiments than the bare minimum $n - 1$ to improve the accuracy of the diffusion matrix [6]. Typically, noise can be a critical impediment when the diffusion matrix is ill-conditioned because of the coexistence of several diffusion mechanisms (corresponding to several eigenvectors) with very different eigenvalues. In such a case, small experimental errors have dramatic consequences on the minor eigenvectors (with smaller eigenvalues) even though the dominant eigenvectors are not so badly affected.

4.4 Uphill Diffusion

The ultimate manifestation of diffusive coupling in a multicomponent system is the particularly striking *uphill* diffusion of a component against its own concentration gradient. This effect can be understood only with the Fick–Onsager equations. Uphill diffusion of an element i typically occurs when off-diagonal terms of the diffusion matrix and concentration gradients of several components j are large. In this situation, the diffusive flux of i resulting from its higher concentration is overwhelmed by the effects of the off-diagonal coupling terms.

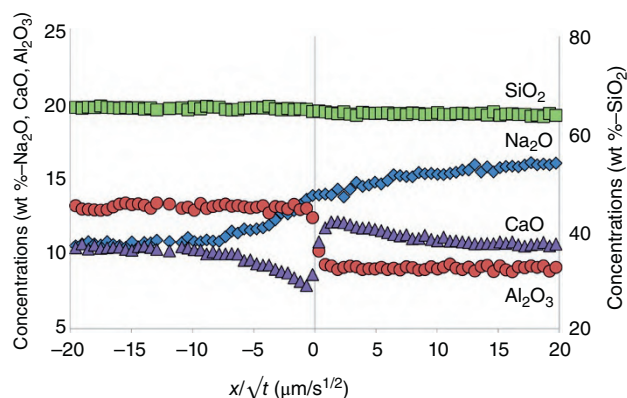


Figure 2 Uphill diffusion of CaO in the concentration profiles collected during chemical diffusion in the NCAS quaternary system at 1200 °C for one hour [6].

The initial concentration gradients then locally increase during diffusion (Figure 2). Since all compositional gradients have been erased at equilibrium, the phenomenon is necessarily transient but it is nonetheless important because it considerably affects melt homogenization. An intuitive way to understand this process is to view a component as “dragged along” by other components. This picture may be misleading, however, in that, the true driving force for diffusion is the chemical potential gradient. Consequently, if activity gradients are plotted instead of concentration gradients, then the anomalous uphill profile disappears because all components are actually going down their own gradients in the thermodynamic (activity) space (Figure 3).

4.5 Diffusion Path

From a theoretical standpoint, the thermodynamic description given by Eqs. (8) and (9) in addition provides one with interesting insights onto the diffusion and thermochemical pathways followed by the system in the

compositional space. A graphical view of chemical diffusion and of the couplings that characterize it is obtained with plots of chemical compositions along diffusion profiles (Figure 4). As long as the assumption of a semi-infinite medium is valid, the two end-members of the diffusion couple are then easy to show. The composition of the interface also lies along a straight line joining these end-members and represents their average composition. This plot is called a *diffusion path* because it displays the composition-time trajectory followed by any point of space (as long as diffusion has not reached the boundaries of the sample). In the absence of coupling between the components, all compositions plot along the straight line joining the end-members (Figure 4). Conversely, when diffusive coupling is significant, the trajectory is not a straight line but takes a symmetrical S-shape when the diffusion matrix does not depend on concentration (Figure 4).

This view is also of interest because it graphically represents eigenvalues and eigenvectors of the diffusion matrix $\mathcal{D}$ [4]. Typically, the two coplanar vectors determining the orientation of the S-shaped diffusion path are the eigenvectors of $\mathcal{D}$. Furthermore, the diffusion path close to the end-member compositions is colinear with the major eigenvectors (i.e. those with the largest eigenvalue) because the fastest exchange process will dominate during the early stages of diffusion. On the diffusion path, this fast reaction will thus dominate for compositions close to the end-members (Figure 4). The plot of the diffusion path is, therefore, a simple way to identify the exchange reactions at work during chemical diffusion.

5 Available Chemical Diffusion Data

5.1 Identified Couplings

Experimental determinations of the diffusion matrix are few for multicomponent oxide systems. A comprehensive discussion of the published data can be found in [15] for

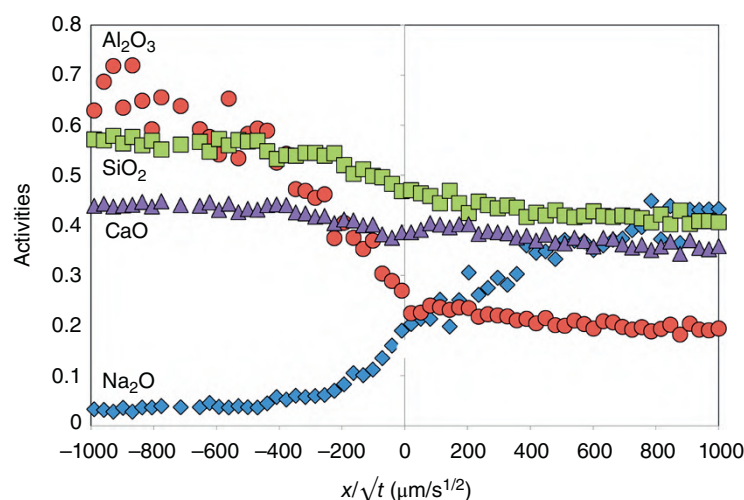


Figure 3 Diffusion profiles of Figure 2 represented in the activity space, no longer showing uphill diffusion [6]. Activities calculated with the FactSage thermodynamic program (Chapter 5.3) and rescaled to fit on the same figure ($\times 10^9$ for Na₂O, $\times 10^5$ for Al₂O₃, and $\times 10^4$ for CaO).

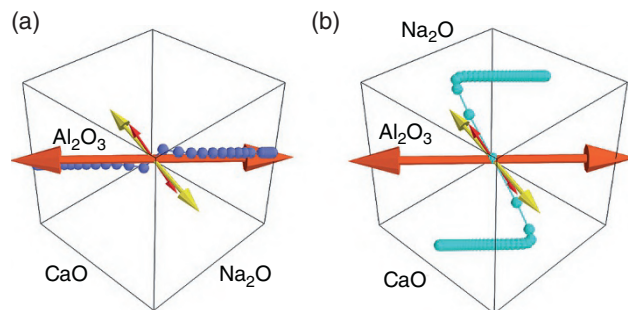


Figure 4 Diffusion paths viewed in 3-D around a single melt composition in the NCAS quaternary system [6]. (a) Diffusion of Na_2O versus CaO , essentially controlled by only one exchange reaction, represented by the large red arrow. (b) Diffusion of Na_2O versus Al_2O_3 , controlled by two exchange reactions represented by the thin and bold vectors indicated, respectively.

binary systems and in [14] for diffusion matrices. The ternaries $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (CAS) and $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (MAS) and the quaternary $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (CMAS) are relatively well-characterized systems because they contain key components of natural and industrial melts and glasses. Despite the relatively inconsistent nature of the earliest studies [16–19], some common features are observed. As expected, chemical diffusion in molten CAS, MAS, and CMAS shows clearly diffusive couplings among the oxide components (uphill diffusion profiles). This coupled chemical diffusion between CaO and SiO_2 and MgO and SiO_2 makes their respective diffusion distances comparable to one another (e.g. [20]; 7).

In general, large concentration gradients in alkaline-earth oxides accelerate the counter-diffusion of SiO_2 (Figure 1), whereas the nature of the coupling depends markedly on melt composition. Typically, the flux of SiO_2 is strongly coupled to the concentration gradients of CaO and MgO in polymerized melts. On the other hand, the flux of Al_2O_3 is preferentially coupled to the concentration gradients of CaO and MgO in depolymerized melts. Furthermore, the sign of the coupling of CaO and MgO with either Al_2O_3 or SiO_2 reverses between polymerized and depolymerized compositions. The fluxes of CaO and MgO are positively coupled to the concentration gradients of SiO_2 in siliceous compositions, whereas they are negatively correlated in silica-poor compositions. Finally, it is generally observed that the diffusive behaviors of CaO , FeO , and MgO are very similar in a given melt [14, 21]. It is thus reasonable to consider $\text{CaO} + \text{MgO} + \text{FeO}$ as a single component in the absence of a complete diffusion matrix.

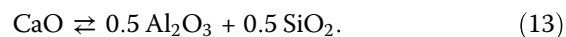
Chemical diffusion of alkali cations has also been studied in various systems such as $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (KAS), $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, $\text{K}_2\text{O}-\text{SrO}-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ (NCS), and $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (NCAS) [6, 21–25]. As for alkaline-earth-bearing

systems, the experiments point to significant coupling. The diffusive flux of Na_2O is strongly and negatively coupled to the concentration gradients of SiO_2 and CaO . Interestingly, in the quaternary $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, Na_2O is primarily coupled to CaO and mainly decoupled from the motion of network formers [6]. Turning to the flux of K_2O , it seems moderately to weakly coupled to the gradients of SiO_2 . Again, the silica content has a strong control on the sign of the coupling. The diffusive flux of SiO_2 is only weakly coupled to the concentration gradients of Na_2O in basaltic (silica-poor) melts, but strongly and negatively coupled to the concentration gradients of the alkalis in silica-rich melts. Finally, the diffusion experiments of [25] also suggest that the diffusive behavior of water in multicomponent liquids is similar to that of Na_2O : the diffusive flux of water is negatively and strongly coupled to the concentration gradients of silica.

A direct comparison between the magnitude of the eigenvalues of the diffusion matrices in alkali- and alkaline-earth-bearing simple systems is greatly hampered by the limited data sets available. At a given temperature, it nonetheless seems that eigenvalues are from 1 to 4 orders of magnitude higher in molten CAS, CMAS, and MAS than in KAS. This is consistent with the tighter bonding of tetrahedral aluminum with potassium than with calcium and magnesium as charge-compensating cations, which thus results in an overall lower mobility of potassium [14].

5.2 Diffusion Paths

As noted in [24], each eigenvector of the diffusion matrix can formally be written as an exchange reaction between species, the coefficients of the eigenvectors determining the stoichiometry of the reaction. For example, in the CAS system, an eigenvector of coefficients (1, -0.5 , -0.5) in the basis $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ is equivalent to the reaction



This reaction is consistently found in various compositions of the CAS, MAS, and CMAS systems [7, 19], suggesting that alkaline earth elements move through the aluminosilicate network by breaking $\text{Al}-\text{O}-\text{Si}$ linkages. Such microscopic insights on diffusion mechanisms demonstrate the power of the diffusion-matrix approach: with an appropriate mathematical apparatus, exchange reactions at the microscopic level can be obtained from macroscopic measurements of concentration profiles. Another major reaction has been identified in the NCS and NCAS systems, namely, the exchange of sodium and calcium (e.g. [5, 6]). It probably takes place in the modifier-rich channels described by Greaves

(Chapter 2.5), which represent preferential migration pathways for these cations. Because this migration does not involve the breaking of bonds formed between oxygen and network formers, the eigenvalue of the exchange of sodium and calcium is significantly larger than those of reactions involving network formers.

Interestingly, the diffusion matrices obtained in quaternary systems [6, 19] suggest that exchange reactions of simple (i.e. ternary) systems can often be transposed to more complex systems. Such results are consistent with the essentially pairwise nature of interatomic potentials (Chapter 2.8) and, thus, with the fact that eigenvectors point to the collective rearrangements that dominate mass transport (because a given mechanism will be faster and energetically more favorable than others). Nonetheless, several questions remain open about the interpretation of eigenvectors in terms of exchange mechanisms, such as why eigenvectors vary or not when composition changes.

5.3 Temperature Dependence

The temperature dependence of the elements of diffusion matrices has received less attention. The available data focus on the CAS, CMAS, and KAS systems [9, 14, 16, 24], but they have unambiguously shown that the eigenvalues obey simple Arrhenius laws. Even though these eigenvalues vary with composition by more than five orders of magnitude at a given temperature in the CAS system, the activation energies are relatively constant at around 200–220 kJ/mol. These values are also very close to the activation energies for the self-diffusions of Si and Ca in similar melts (e.g. [3, 7, 16, 17]) and to the typical activation energies for viscous flow (Chapter 4.3). The temperature dependence of the $\mathcal{D}$ eigenvalues in the KAS system is more complicated. In that case, the activation energies of the two eigenvalues are very different. This feature likely highlights the fact that SiO₂ and CaO are strongly coupled in CAS. On the contrary, in the KAS system, the diffusive flux of K₂O is less coupled to the concentration gradient of SiO₂.

Turning finally to the eigenvectors of the diffusion matrices at a given melt composition, we note that they do not seem to be very sensitive to temperature. This near constancy may thus suggest that diffusion paths persist over large temperature intervals. If true, this observation would make a systematic survey of these paths even more important to develop an empirical and practical description of chemical diffusion in multicomponent melts.

6 Perspectives

Modeling of multicomponent diffusion will greatly benefit from a better description of the activity–composition relations in molten systems. Improved thermochemical

descriptions of melts will certainly help to describe molecular interactions at the origin of uphill diffusion. Before such a comprehensive approach is available, however, a reasonable set of experiments focused on a few important quaternary systems should assess the persistence of eigenvectors over a wide range of compositions, temperature, and pressure. This would be a major achievement because available data suggest that vectors defined for simple systems are preserved when additional components are added. Since these eigenvectors are related to local exchange reactions, their persistence would clearly help bridging the gap between structural and kinetic aspects of glass-making melts. The signatures of these reactions could then be probed either by molecular dynamics or first-principle simulations. In addition, in a near future, the exchange rates computed from *in situ* NMR measurements could be compared with the characteristic kinetics of such local reactions to assess the overall self-consistency of the structural and kinetic models.

Acknowledgments

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4.5

Thermal Diffusivity and Conductivity of Glasses and Melts

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1 Introduction

The rate at which heat moves through a glass has fundamental implications in both industry and geology. In glassmaking, for instance, thermal conductivity controls the rate at which flat (Chapter 1.4) or hollow (Chapter 1.5) glass is shaped at high temperature. In geology, it determines the rate of cooling of ascending magma, the longevity of magma chambers, and the extent of welding by which glassy volcanic ash gives rise to dense rock (Chapter 7.2). Because the rate of heat transfer within a phase is characterized by its thermal conductivity (k) and thermal diffusivity (D), these properties need to be known as a function of temperature and chemical composition if heat transfer is to be understood in a quantitative way in a variety of fundamental or applied contexts.

Over a microscopic scale, thermal energy is transferred via either *conduction* or *radiation* in response to an imposed thermal gradient. Heat can also be transported by *advection* where moving mass elements of a body each carry heat according to their heat capacity and temperatures. The macroscopic process of *convection* combines conduction, radiation, and advection, so it constitutes a system-wide response achieved under particular conditions rather than a fundamentally different heat-transfer mechanism.

To decipher the complex process of heat transfer, the first step is, therefore, to examine the two basic processes of conduction and radiation. This will be done at the beginning of this chapter where particular emphasis will be placed to define rigorously both processes and to review their microscopic origin. We will then describe in some detail how heat-transport properties are

measured because of the possible experimental pitfalls that have caused confusion in the literature. Finally, we will review the aforementioned temperature and composition dependences of these properties and point out some correlations they show with other physical properties of glasses and melts.

2 Theory

2.1 Thermal Conductivity and Diffusivity

The thermal conductivity (k) of a body relates temperature (T) and heat flux (F) by Fourier's law:

$$F = -k \nabla T. \quad (1)$$

For heat conduction in an isotropic medium under isobaric conditions, one has

$$\rho C_p \frac{\partial T}{\partial t} = k \nabla^2 T + Q + \frac{\partial k}{\partial T} \left[\left(\frac{\partial T}{\partial x} \right)^2 + \left(\frac{\partial T}{\partial y} \right)^2 + \left(\frac{\partial T}{\partial z} \right)^2 \right]. \quad (2)$$

where ρ is the density of the body, C_p its heat capacity at constant pressure (P), and t time and Q describes internal heat sources such as radioactivity or viscous heating. The nonlinear form of Eq. (2) provides feedback between k and T because k depends on temperature in a complex way.

With some techniques one measures instead the thermal diffusivity, from which k can be determined from the definition

$$k_{\text{lat}} = \rho C_p D, \quad (3)$$

where C_p and ρ are generally available or can be estimated with reasonable accuracy (see Chapters 3.5 and 3.6). Historically, the focus has been on k , which is complex

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compared with D , because heat capacity depends strongly and in a complicated manner on T . Over a temperature range sufficiently narrow that the physical properties are effectively constant, if Q is zero, then Eq. (2) takes on a simple form whereby thermal diffusivity alone governs the temperature–time evolution:

$$\frac{\partial T}{\partial t} = D \nabla^2 T. \quad (4)$$

2.2 Conductive Heat Transport

Below about 800 K, the transfer of heat from or to a body is governed predominantly by conduction if one neglects transient thermal events and the experimental difficulties associated with the high transparency of glasses. In an electrically insulating solid, the so-called lattice conductivity (k_{lat}) has been considered to be the main mechanism, involving scattering of *phonons* (Figure 1, top), which are quantized lattice vibrations ($k_{\text{ph,sc}}$). Over unit-cell distances, their characteristic speed is similar to the velocity of sound in the body. At low temperature (<30 K), the thermal conductivity of glasses is modeled in the same manner as for crystals wherein phonon scattering models are based on Debye’s concept of the phonon gas. Because different variations of k with T are observed for crystals and glasses at higher temperatures, however, existing models have considered that different mechanisms operate in disordered glasses [1]. However, the temperature dependences of D for glasses and crystals are similar up to the glass transition temperature [2], and thus the “glass-like” behavior, where k increases from cryogenic temperatures up to a plateau, results from the strong increase in heat capacity with T that overwhelms the weak decrease in D as T increases (Eq. (3); data

provided below) and not necessarily from a different mechanism.

The lattice thermal conductivity in phenomenological models is calculated from

$$k_{\text{lat}} = \frac{1}{3} \rho C_V u \Lambda, \quad (5)$$

where C_V is the isochoric heat capacity, u is the velocity of phonons or elastic waves, and $\Lambda = \tau u$ is the mean free path of phonons with a mean lifetime τ . The concept originated with Debye, but the estimation of phonon lifetimes or mean free paths remains the most uncertain part of the modeling.

For glassy materials, the plateau in k has been modeled with the assumption that the harmonic motions of neighboring atoms are uncorrelated. Einstein’s model of vibrations in solids has been found adequate for a variety of complex glasses [1]; however, its underlying assumption, i.e. that no coherence exists between motions of neighboring atoms, is questionable. Other phenomenological models concern scattering from two-level states and tunneling. Owing to uncertainties in phenomenological models, C_p is often substituted for C_V in order to make use of measured properties in the computation.

To describe the change of k with temperature, more complex, first-principles models are currently used. Both the Kubo–Greenwood approximation and molecular dynamics have been applied to amorphous Si (see summary by Lee et al. [3]). The former involves calculation of the heat currents (fluxes) between harmonic states when thermal energy and thus temperature vary through changes in vibrational quantum numbers. With molecular dynamics (Chapter 2.8), one can explicitly incorporate anharmonicity and specifically account for temperature-dependent structural changes.

Recently, Hofmeister et al. [2] have proposed that an additional mechanism exists, wherein heat is diffused radiatively at infrared frequencies but at slow phononic speeds by bulk phonon polaritons. This mechanism is manifest in experimental data at high temperature wherein D increases with T for both crystals and glasses. For further discussion and a new model see [4].

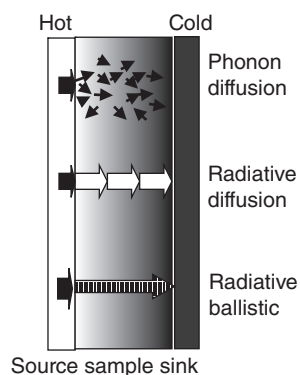


Figure 1 Schematic of radiative transfer. Thick black arrows show the entry of heat from the source into a sample (shaded to depict a temperature gradient). Top, phonon diffusion. Middle, radiative diffusion requires that light is attenuated over small distances. Bottom, ballistic, or direct radiative transfer, which bypasses the sample, is commonplace in experiments on transparent glasses.

2.3 Radiative Heat Transport

2.3.1 Absorbance

From temperatures higher than about 700–1000 K, a distinct heat-transfer process begins to operate, involving high-frequency photons, and rapidly predominates if the material is transparent (see [5]). Distinguishing such photonic from phononic processes is important because the former is not always a material property as radiative transfer between two bodies depends not only on frequency, temperature, and attenuation of light but also

on the distance involved, over which temperature may change significantly.

When the distance over which the temperature changes significantly is larger than the distance over which light becomes attenuated, heat diffuses radiatively via progressive absorption and re-emission of photons. The process then is represented by an effective thermal conductivity, $k_{\text{rad,dif}}$ (Figure 1, middle), which is calculated from optical spectra, generally with the simplifying assumption of constant sample absorbance. Because diffusion at high frequencies generally requires larger distances than are realized during laboratory measurements of k or D , this phenomenon is limited to geologic processes or to large vats of glass.

Absorbance is the key parameter when dealing with diffusion of radiation. It is defined by

$$a = AL = -\ln\left(\frac{I_{\text{trans}}}{I_{\text{incident}}}\right), \quad (6)$$

where A is the absorption coefficient, L the thickness of the material, and I_{trans} the light transmitted (not including reflection losses), which is measured with respect to I_{incident} , the light entering the crystal. “Optically thick” conditions generally hold if the absorbance is greater than 2 but not so large that the medium is opaque (i.e. that some small amount of light exits the sample). For heat-transport problems, an additional stipulation is that the distance over which temperature changes is large compared with the distance required for optically thick conditions (Figure 1, middle). Diffusive conditions thus exclude direct or ballistic radiative transfer, which occurs under optically thin conditions of $AL < 1$, and when light crosses large temperature differences (i.e. ~ 4 K over the $\sim$ mm distances in laser-flash experiments) (Figure 1, bottom).

2.3.2 Diffusive Radiative Transport

Derivations of the effective thermal conductivity ($k_{\text{rad,dif}}$) associated with an optically thick, nonopaque medium in local radiative equilibrium trace back to Kellett’s [6] attempts to understand heat transport in glass furnaces. Kellett [6] and subsequent workers assumed that light enters the solid as a point, forming a cone of diffracted radiation. Instead, entry occurs across a planar surface, and in view of the second law of thermodynamics, heat transfer only occurs down the thermal gradient, and so the historical work includes an erroneous factor of n^2 , where n is the index of refraction, in the effective thermal conductivity. Correcting for this error gives

$$k_{\text{rad,dif}} = \frac{16\sigma T^3}{3A}, \quad (7)$$

where σ is the Stefan–Boltzmann constant. Although this equation is not correct in detail for other reasons, it does

show that radiative effects are most important at high temperature. Importantly, Eq. (7) requires that the absorption coefficient be independent of frequency and temperature (see summary by Choudhary and Potter [7] and the revised model in [4]).

Neither optically thick conditions nor constant absorbance applies to glasses. Experimentally, silicate glasses are optically thick only in the infrared and ultraviolet. Obviously, colorless glasses are transparent in the visible, and this high transparency extends downward in frequency to just above the infrared (the near-IR). Similarly, colored glasses (Chapter 6.2) are commonly transparent in the near-IR. This problem of low A occurring in certain spectral regions creates extremely large values of $k_{\text{rad,dif}}$ so some average of A is used instead. Commonly the Rosseland mean absorption coefficient is used, which is weighted using Planck’s blackbody function:

$$I_{\text{bb}}(\nu) = \frac{2h\nu^3}{c^2} \left[\frac{1}{\exp(h\nu/k_B T) - 1} \right]. \quad (8)$$

where h is Planck’s constant, ν frequency, c the speed of light, and k_B Boltzmann’s constant. However, the Rosseland formalism does not address the underlying issue that glasses are not optically thick in certain frequency regions, which in turn means that radiation is *not* diffused but carried ballistically (see Section 2.3.3). Although more precise formulations than Eq. (7) exist, they are not commonly applied because they require specific knowledge of A from infrared to ultraviolet frequencies for the glass of interest (see Choudhary and Potter [7] for a summary of absorption data and a discussion of the problems). The same fundamental problem exists in the more precise formulations, namely, that A being near zero in any frequency range violates the diffusive approximation, and so the formulation is not relevant.

2.3.3 Ballistic Radiative Transport

Neither Eq. (7) nor its more precise alternatives address properly the problem of transparency of glasses in laboratory experiments. When temperature gradients are steep, light from the source can warm the measuring thermocouple with scant participation of the medium (Figure 1, bottom). This process is termed boundary-to-boundary, direct, or ballistic and is especially important in transient experiments where radiative transfer dominates the initial response of the system to the input of heat because of the tremendous speed of light.

This ballistic radiative transfer takes place in *optically thin* samples and depends on the experimental conditions, whereas diffusive radiative transfer operates in *optically thick* samples and is a material property. Distinguishing the two processes can be difficult, however, because both are governed by Planck’s blackbody

function, so they can operate at the same time, and also because glasses are transparent at high frequencies over mm to cm scales. As a result, confusion between the two has led experimental data on solids to be often misinterpreted, both historically and recently, which has adversely affected our understanding of the thermal conductivity of glasses and melts.

A model of ballistic radiative transport for use in laser-flash analysis experiments provided by Hofmann et al. [8] is widely used in data analysis. Its details are beyond the scope of this chapter, but in essence its equations are fitted to the raw temperature–time data, permitting extraction of thermal diffusivity for small temperature differences, after Eq. (4). The model does not require knowing optical properties.

Other methods of measurement, particularly transient, are affected by ballistic radiative transport. No simple formula exists for optically thin conditions (Figure 1, bottom). In an attempt to remove radiative effects from the data, some researchers have reduced the total measured thermal conductivity by using equations intended to describe diffusive radiative transfer as described here and in Section 3. This approach can only provide a very rough estimate of ballistic radiative effects, with uncertainties exceeding a factor of 2.

2.4 Characteristic Speeds of Microscopic Mechanisms

All solutions to the temperature–time Eq. (4) have the form

$$D \sim L^2/t, \quad (9)$$

where t is a characteristic thermal timescale. Hence, a cooling front moves at a speed $u \sim L/t$. Inserting this approximation into Eq. (9), one then obtains

$$u \sim D/L; \quad (10)$$

so, over short scales, the speed u is that of a disturbance, namely, the compressional velocity (u_p) for conduction and c/n for high-frequency photons. The ratio of the speeds at any given distance holds for all length scales. Hence, the initial response of any system to a transient heat pulse is governed by high-frequency radiative transfer, which is $\sim 10^5$ times faster than conduction. Quasi-radiative equilibrium is rapidly attained, after which phononic conduction governs the temperature evolution.

This conclusion has important implications for heat-transfer experiments. During transient experiments, the time intervals involved are sufficiently short that ballistic radiative transfer has a large impact on the results

regardless of the actual temperature. For steady-state experiments, the slow cooling regime is reached, and so the effect of direct radiative transfer depends on the flux, which in turn depends strongly on the temperature in accord with Planck's function (Eq. 8). Thus, for cryogenic temperatures, steady-state experiments are less affected by direct radiative transfer.

3 Measurement Techniques

For measuring thermal transport properties, transient methods generally provide D , whereas steady-state variants yield k . Even though many such methods exist, we will deal with those that have been applied to glasses or are widely used and will also mention new developments that are promising for future glass research. Because the molten state is of particular interest, the focus will be on high-temperature (≥ 300 K) methods, whereas discussion of low-temperature measurements will be omitted. Absolute values are a concern because problems such as radiative transfer and contact losses differ with different techniques, which make it difficult to benchmark them. Owing to the experimental difficulties and inconsistencies in the data (especially at high temperature), we aim at providing enough details such that the potential shortcomings of each method can be understood. For a thorough analysis, see [4].

3.1 Contact-Free Methods

Laser-flash analysis [9] is commonly applied to diverse materials. For glasses it is advantageous because contact losses are absent and ballistic radiative transfer associated with sample transparency can be removed with the model of Hofmann et al. [8].

A sample in the form of a small, thin slab (~ 0.3 – 3 mm thick by 6 – 15 mm diameter) is held at temperature in the furnace (Figure 2, inset). Additional heat is supplied remotely by an IR laser pulse to a thin graphite coating on the bottom of the slab. As the increment of heat migrates to the top of the sample, which is also graphite coated, the surface temperature of the slab rises, and its emission increase is recorded by the IR detector (Figure 2). The detector response is known as a temperature–time curve. Additional metal coatings (Au or Pt) beneath the graphite can be used to suppress radiative transfer, but they tend to perturb the measurement for materials such as glasses that have low D values [10].

For the simplest case of adiabatic heating, without any radiative heat transfer [9],

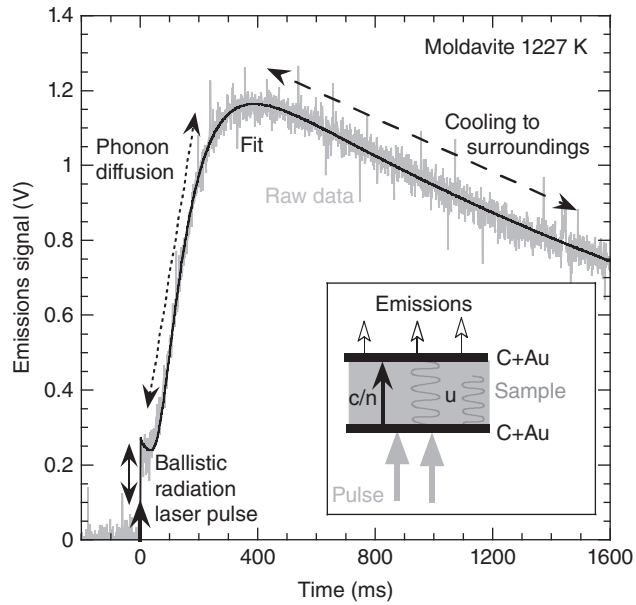


Figure 2 Time-temperature curves and schematic of LFA experiments. Gray curve: raw data for moldavite glass. Heavy arrow: laser pulse. Solid line: Hoffman et al.'s [8] model, with processes as indicated. (Inset) Physical transfer of heat during the experiment. Emissions (light arrows) from the top graphite coat are recorded by an infrared detector. After the laser pulse (heavy gray arrows) is absorbed by the bottom coat, this heat then either traverses the sample as photons (medium arrow) near light speed, c/n , or as phonons (squiggle arrow) near sound speed, u , both increasing emissions.

$$D = 0.1388 L^2 / t_{\text{half}}, \quad (11)$$

where L is sample thickness and t_{half} is half of the time required for temperature to reach the maximum after the laser pulse. In the absence of radiative transfer, the main uncertainties arise from sample thickness and deviations from truly planar and parallel faces. Experimental uncertainties of $\pm 2\%$ have been inferred for measurements of D_{lat} from benchmarking against graphite or iron. But graphite properties can vary from one sample to another, so the development of standards and round-robin testing is needed with homogeneous materials that are not transparent and thus can be accurately measured with other techniques.

At very high temperatures, data can be collected on suspended glass disks, even above the glass transition, until the sample viscosity becomes sufficiently low for flow or crystallization to occur [10, 11]. Thermal diffusivity of melts in containers has also been measured. In that case, however, overly large values have been obtained because available models of the time-temperature signal account either for radiative transfer or for the contribution of the finite thickness of the container, but not for both effects.

In a variation of the laser-flash method, the reflected signal from the base of a platinum crucible containing molten glass is analyzed, which essentially represents a thermoreflectance technique whose main advantage is that problems with bubble formation and retention are avoided. With this technique, Shibata et al. [12] studied Na-Ca-Si oxide glasses used as research standards for diverse properties. When interpreting the time-temperature curves, they did not account for ballistic radiative transfer, which does not seem to play a role in reflection experiments. Although they did not benchmark their method, their results are comparable with data on similar compositions measured with the standard LFA technique (Figure 3).

3.2 Conventional Techniques Involving Physical Contacts and Direct Heating

Except in recent work, most studies of $k(T)$ or $D(T)$ have utilized conventional techniques wherein a heat source and/or thermocouples directly contact the sample (see review [5] and also the data summarized by Choudhary and Potter [7]). Common features of contact methods are upper temperature limits of about ~ 1200 K, long measurement times, radiative heat losses from the surface, variable amounts of ballistic radiative transfer, and contact losses at the interfaces that cannot be avoided

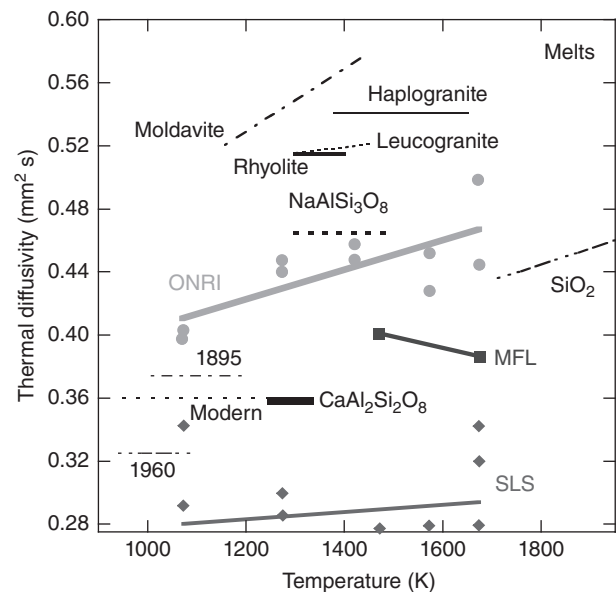


Figure 3 Laser-flash analysis data on D of melts. Compositions in Table 1. Symbols with least squares fitted lines from Shibata et al. [12]. Lines without symbols are data in Hofmeister et al. [11] and references therein. Except for MFL, moldavite, and leucogranite with 1–2 wt % FeO, these glasses have negligible iron contents.

through surface polishing (see below). To determine k , steady-state methods are generally used, which require information on both the flux and the temperature gradient, Eq. (1); in addition, boundary conditions and sample geometry influence the results. Obtaining D involves transient methods wherein the time that a thermal disturbance takes to travel a certain distance is measured (Eq. 4). Some techniques provide both k and D . Examples are the transient hot-wire and hot strip methods, which have uncertainties of ± 6 and 30%, respectively.

Conventional measurements on hard crystalline solids commonly differ by $\pm 20\%$ even at room temperature. Data on glasses vary by a similar amount. Offsets existing between various data sets collected on similar materials by different authors are consistent up to 500–700 K, whereupon $\partial k/\partial T$ changes sign. Trends are less regular at higher temperatures. Both of these high-temperature discrepancies are due to variable amounts of unwanted, ballistic radiative transfer. Particulars of the experiments (e.g. contact adhesives, sample thickness, and absorption characteristics) are likely causes of the variation in the position and degree of the upturns in $k_{\text{meas}}(T)$. Radiative effects are reduced if absorption from the visible to near-IR is strong (e.g. glass with coloring dopants). Some researchers have attempted to separate phonon from photon components by subtracting $k_{\text{rad,dif}} \sim cT^3$ (or other approximations) from the measured k to obtain k_{lat} [5]. This approach is very approximate because optically thick conditions are difficult to achieve experimentally in the near-IR region, so the radiative transfer is not diffusive but ballistic and cannot be accounted for by Eq. (7). The correction is large even for darkly colored glasses [14].

An additional source of error arises from systematic losses that occur in conventional measurements because of the aforementioned thermal-contact resistance. This impediment can be described as a thermal resistance, r_{th} , which is the inverse of the thermal conductivity of the interface. Because thermal resistances in series add, one has

$$\frac{1}{k_{\text{meas}}} = \frac{1}{k_{\text{sample}}} + r_{\text{th}}. \quad (12)$$

So contact measurements set a lower limit on k measurements at 298 K in the absence of other problems. Rewriting Eq. (12) one obtains

$$D_{\text{meas}} \sim D_{\text{true}} / (1 + D_{\text{true}}/D_{\text{contact}}). \quad (13)$$

Copper with $D = 111 \text{ mm}^2/\text{s}$ is commonly used as a heating element. Because D of the contact is a blend of the two substances, it lies between D of the metal and that of insulator (i.e. D_{contact} is $\sim 50 \text{ mm}^2/\text{s}$), and the loss should be $\sim 10\%$ per contact.

3.3 Periodic Contact Techniques

This type of method involves application of a heat pulse to probe the immediate response of the system, which generally gives rise to strong ballistic radiative transfer. Ångström's method or its variants are widely used. In brief, a sinusoidal source of heat at frequency ω is applied to one end of a rod-shaped sample, and the phase of the decaying sinusoidal temperature wave that passes through the sample is measured at a distance L along the rod. Solutions to Fourier's equation in one dimension show that the phase depends on $L(\omega/2D)^{1/2}$. Correction terms address boundary conditions such as surface losses via radiation to the surroundings, but other errors stem from the presence of the smaller diameter thermocouple wire inserted in a hole drilled at the center of the sample. The hot-probe technique is similar, involving measuring the temperature rise created by a long linear heat source embedded in a medium.

The 3ω method (Cahill and Pohl [13]) involves a single contact. Thermal conductivity is determined below about 750 K with a third-harmonic detection scheme from the self-heating of a narrow metal line deposited on the sample. This radial method mixes two polarizations. An important advantage is insensitivity to blackbody radiation. Slightly lower values for silica are seen with the 3ω method than with laser flash (Figure 4), but this difference might alternatively be attributed to sample differences rather than to inconsistency between the methods.

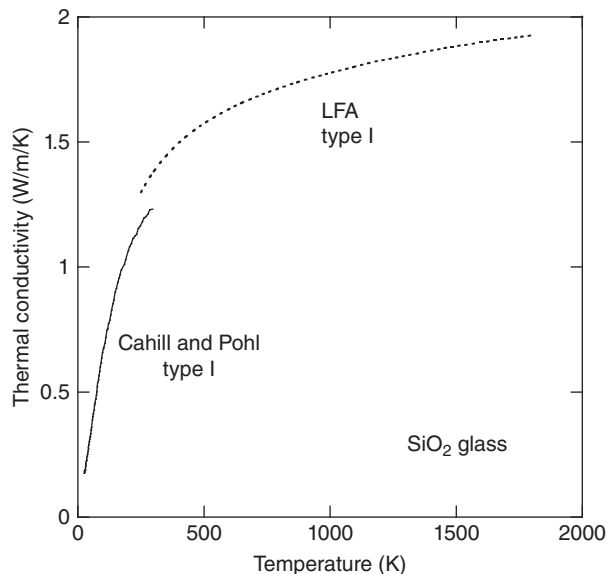


Figure 4 Comparison of k for type I SiO_2 glass (slightly oxygen-deficient fused quartz with negligible water content) from radiation-free methods. Dotted line = LFA [10]. Solid line = 3ω technique [13].

3.4 Steady-state Contact Techniques

In steady-state experiments, such as the divided-bar method, radiative transfer should be unimportant. This is true at low temperature, but not at very high temperature where the high radiative heat flux makes quasi-radiative equilibrium difficult to achieve over the duration of experiments. Linear and radial geometries are used wherein the heater is separated from the receiving thermocouple.

3.5 Contact Techniques That Are Neither Transient, Periodic Nor Steady-state

An example is the glass-metal contact method ([14]), which has promise for molten materials. In this technique, a metal probe at a temperature different from that of the glass is inserted, and the coefficient of heat penetration = $kC_p\rho$ is determined directly from fits made to the asymptotic temperature jumps or drops recorded during the experiment. The method is relatively insensitive to radiative transfer. Although the results agree with LFA analyses for soda-lime glass of similar compositions, they show more scatter (Figure 5). Another example is the hot-wire method, which has been applied to slags [5, 15], as discussed below.

4 Thermal Diffusivity and Conductivity Data: Key Variables

Low-temperature heat transport studies of diverse glassy substances such as amorphous Si are found in the physics literature (cf. [1, 13]). Data at higher temperatures, mostly on silicate glasses, exist in the Earth and materials science articles [10, 11, 14], whereas results for the molten state, particularly Ca–Al slags, are found in engineering reports

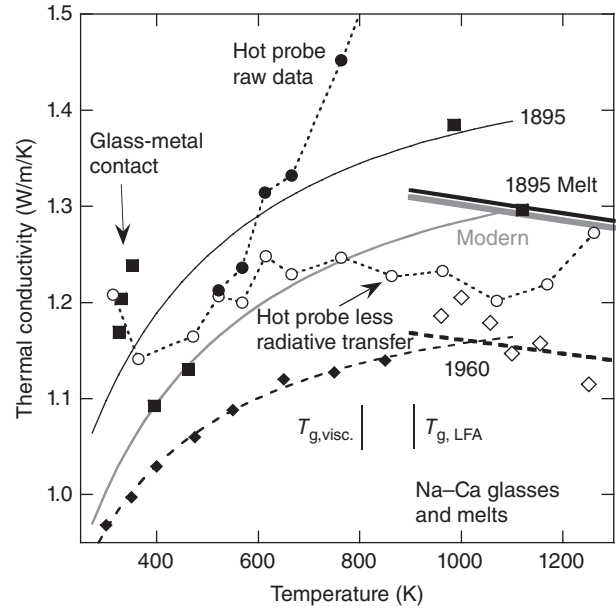


Figure 5 Comparison of k at high temperature from LFA to contact techniques. Curves: soda-lime glasses [11] listed in Table 1. Diamonds show the uncertainty arising from thermal diffusivity measurements for one sample. Squares: data from Tempel et al. [14] with a metal probe technique on a glass that is similar to 1895. Vertical lines: glass transition temperatures from viscometry and in LFA experiments (see text).

[5, 7, 15]. We list data on D and k in Tables 1–3, with a focus on high-temperature results, namely, those obtained from room temperature to the glass transition and beyond, these selected data being representative of the range of chemical compositions and structures examined by LFA [10, 11, 16–18]. Purposely, we have limited ourselves to LFA studies of bulk samples from which radiative transfer effects have been removed to make direct comparison between sample properties. We will then take additional advantage of the fact that these

Table 1 Glass chemical compositions.

	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	FeO	MnO	Cr ₂ O ₃	TiO ₂	Sum
Albite	67.14	21.21	11.43								99.78
Anorthite	42.08	37.26				19.86					100.00
Diopside	54.82				16.55	25.58					97.0
Rhyolite	76.53	12.92	3.81	4.69	0.02	0.97	0.99	0.06		0.07	100.06
Moldavite	80.25	9.86	0.37	3.45	1.87	2.46	1.53	0.06	0.005	0.30	99.56
NaCa1985	72.59	2.85	15.95	0.90	1.5	6.69	0.36	0.01		0.10	100.96
NaCa1926	74.7	0.44	12.03	0.12	0.45	12.60	0.11	0.01	0.006	0.03	100.84

Some of the totals differ from 100% because of analytical errors.

Source: Data sources from [10, 13], and references therein.

Table 2 Thermal diffusivity values and fitting parameters for selected glasses and liquids.

Sample	Composition	D_{298} mm ² /s	$D = FT^{-G} + HT$			$T_{\text{fit,max}}$ K	D_{melt} mm ² /s	T_{melt} K
			F	G	$H \times 10^5$			
Silica	SiO ₂ (anhydrous infrasil)	0.87	6.1135	0.35773	16.635	1600	0.265 + 0.0001 T	1700–2000
Albite	NaAlSi ₃ O ₈	0.62	3.3943	0.3095	11.996	1300		
Albite		0.637	3.1418	0.29188	11.762	1300	0.5	1300–1500
Anorthite	CaAl ₂ Si ₂ O ₈	0.58	2.2635	0.24808	6.7805	1200	0.358	1300
Diopside	CaMgSi ₂ O ₆	0.532	2.9726	0.31265	7.7594	1000	0.29	1100–1200
Rhyolite	Na _{0.36} K _{0.29} Ca _{0.05} Fe _{0.04} Al _{0.74} Si _{3.73} O ₈	0.633	2.9587	0.28256	12.647	1260	0.52	1350–1450
Moldavite	Na _{0.09} K _{0.19} Ca _{0.11} Mg _{0.12} Fe _{0.05} Al _{0.49} Si _{3.44} O ₈	0.684	9.9309	0.49603	27.168	1150	0.347 + 0.000157 T	1280–1480
NaCa1895	Na _{1.40} K _{0.05} Ca _{0.33} Mg _{0.10} Fe _{0.02} Al _{0.15} Si _{3.30} O ₈	0.55	1.1354	0.13133	0	870	0.38	1000–1200
NaCa1926	Na _{1.08} Ca _{0.61} Al _{0.03} Si _{3.39} O ₈	0.53	1.3436	0.16957	0	900	0.35	940–1170

The fits provide D in mm²/s with T in K. Coefficient G has no units. Units of coefficient F depend on the value of G . Coefficient H has units of mm²/sk. χ^2 ranged from 0.0001 to 0.0005. T_{max} is the limit to which all these fits can be projected to. High uncertainties in F are due to tradeoffs in fitting exponent G . All digits shown needed to reproduce the data.

Source: Data sources from [4, 9, 10, 13], and references therein.

Table 3 Thermal conductivities of selected glasses and liquids.

Sample	k_{298} W/m K	$k = a + bT + cT^2 + dT^3 + eT^4$					$T_{\text{fit,max}}$ K	k_{melt} W/m K	T_{melt} K
		a	b	$10^6 c$	$10^9 d$	$10^{12} e$			
Silica	1.373	1.0331	0.0014282	−0.82169	0.1596		1800	0.81 + 3.05 $10^{-4} T$	1600–2000
Albite	1.243	0.92708	0.0013337	−0.999	0.27279		1300	1.666–5.352 $10^{-5} T$	~1200–1500
Anorthite	1.125	0.45381	0.0035458	−5.4675	4.0307	−1.1386	1200	1.471–1.65 $10^{-5} T$	~1100–1500
Diopside	1.236	−0.09697	0.0085558	−18.575	17.872	−6.2768	1000	1.382–1.266 $10^{-4} T$	~1000–1400
Rhyolite	1.170	0.703	0.00202	−1.71	0.57		1200	0.856	~1350
Moldavite	1.166	0.795	0.00158	−1.26	0.49		1100	0.980 + 6.14 $10^{-4} T$	1300–1500
NaCa1985	0.964	0.669	0.00196	−1.95	0.70		900	1.39–0.808 $10^{-4} T$	~900–1200
NaCa1926	1.031	0.695	0.00153	−1.52	0.55		900	1.35–1.08 $10^{-4} T$	~900–1200

Fits differ slightly from the original sources due to restriction of temperature intervals in some cases.

Source: Data sources from [9, 10, 13], and references therein.

measurements involve glasses and melts of the same composition, which will permit another type of comparison to be made. Unfortunately, such measurements of glasses are limited to silicates. Other LFA measurements exist for borosilicate crown glass (*n*-BK7, which consists of 70 wt % SiO₂, with roughly equal amounts by weight of B, Na, and K oxides) and yielded $D(T)$ data similar to those of the other silicate and aluminosilicate glasses presented below. This similarity comes as no surprise, because crown glass is a silicate glass. Other types of glasses exist, such as those that are phosphate based, but heat-transport data has not been obtained from bulk samples for which radiative transfer effects have been

removed. Similarly, data on amorphous silicon is limited to thin films and to low temperatures and does not provide a good basis for comparison of chemical effects.

Before commenting on these results, however, we must briefly mention the effects of inclusions (including crystals and pores), water content, and internal strain because such defects are often present in the samples investigated. For pure silica glass, variations in thermal history and internal strain, for instance, strongly affect D (e.g. [10]), whereas higher water contents cause D_{glass} to decrease and make the glass transition to occur over wider temperature intervals and at lower temperatures. Owing to the importance of thermal history, a spread in D of about

5% occurs for any given chemical type of silica glass (e.g. with Cl or metal impurities). Studies of commercial soda-lime glasses of different ages have shown that greater variability is associated with antique than with modern glasses, which was attributed to inhomogeneities such as the presence of tiny bubbles and to variations in fictive temperature and internal strain induced by different annealing and/or quenching rates [11].

Inclusions, such as bubbles or crystals, have effects on thermal conductivity that can in principle be predicted from effective medium theory. However, an in-depth discussion of this theory and related approaches is beyond the scope of our report, and published applications largely concern crystalline materials. Of particular interest is the effect of bubbles that has not yet been quantified. Qualitatively, in samples with a milky appearance, a large number of bubbles should reduce radiative transfer as a result of scattering. Bubbles should also reduce phononic heat transport, by analogy to the effect of pores on D of crystalline materials. A simple, but not robust approach, is to use the analogy of electrical resistors in parallel:

$$D_{\text{total}} = \frac{1}{\frac{1-\phi}{D_{\text{glass}}} + \frac{\phi}{D_{\text{pores}}}}, \quad (14)$$

where ϕ is porosity. For the bubbles, the thermal diffusivity of water (0.14 mm²/s) can be used. Roughly, ~10% bubbles should then reduce D from 1 to 0.77 mm²/s.

4.1 Temperature Dependence of Thermal Diffusivity and Conductivity

As observed for diverse crystalline materials, e.g. [2], the thermal diffusivity of glasses continuously decreases with increasing temperature before becoming nearly constant at high temperatures (Figure 6). However, for some SiO₂-rich glasses, a slight increase of D with temperature is seen from ~1000 K up to the glass transition [10]. For samples with high Fe²⁺ contents, $\partial D/\partial T$ is distinctly positive above about 800 K (Figure 7). As discussed in Section 4.4, these positive slopes are not due to ballistic radiative transfer, which was removed with Hofmann et al.'s [8] model: its significance is discussed in Section 3.

Although the nominal uncertainty in the LFA technique is $\pm 2\%$, a wider spread is seen in D for repeat runs and runs on samples that should be identical chemically (e.g. albite glass in Table 2). Part of the variation could result either from sample differences or from experimental uncertainties (e.g. glasses must be very thin to avoid development of a thermal gradient greater than 4 K per mm, so Eq. 4 can be applied). For example, D can be affected by dehydration, varying degrees of annealing at high temperatures, and strain induced during rapid

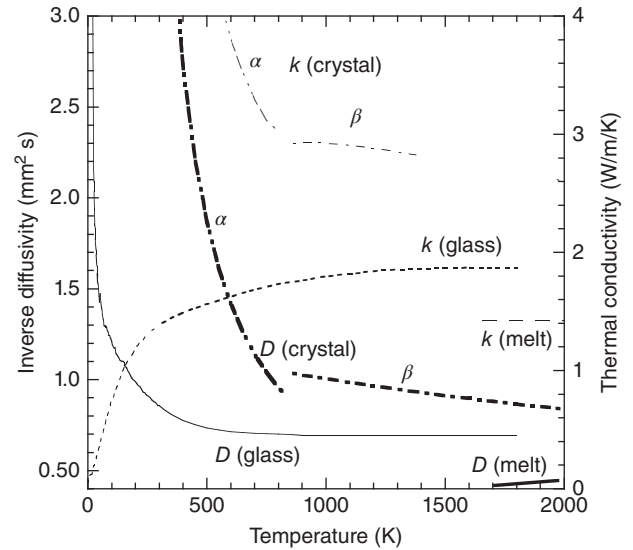


Figure 6 Temperature dependence of thermal diffusivity and conductivity for type I fused quartz (SiO₂ glass: data from [10] and citations therein). Lower temperature results scaled to match LFA results. Quartz crystal polymorphs (labeled α and β) are shown for comparison.

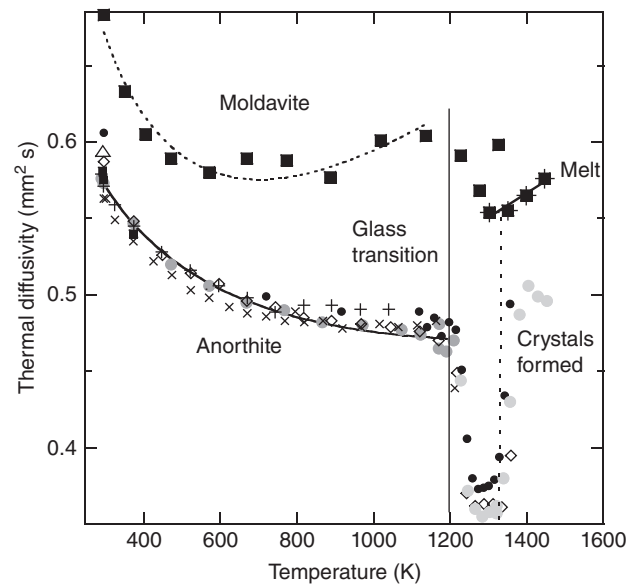


Figure 7 Thermal diffusivity as a function of temperature for moldavite and anorthite, both glasses and melts [11 and citations therein]. Molten anorthite crystallized above 1330 K, causing D to sharply increase.

cooling from high temperature. The variation among identical samples can be attributed in some cases to small but variable amounts of bubbles and crystallites in the samples, as well as to residual strain.

For glasses, k initially has a variation opposite to that of D , increasing steadily from low temperature (Figure 4),

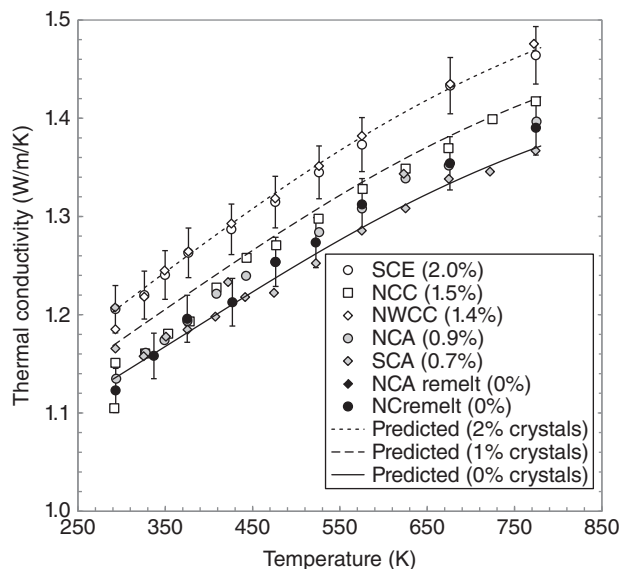


Figure 8 Thermal conductivity of obsidians with different crystal contents. Data are calculated from the product of thermal diffusivity (measured at T), heat capacity (calculated at T), and density at room temperature (thermal expansion introducing a negligible uncertainty). Error bars of $\pm 2\%$ are plotted on symbols for two samples: NCr is a crystal-free remelt, and SCE is the most crystalline sample (2 vol % crystals). Curves are calculated from a least squares fit to the data [16]. Data on remelted, crystal-free glass are provided in the tables.

but, like D (Figure 6), becoming nearly constant at high temperature (Figure 8). As such, k differs much for glasses compared with most crystals for which k first increases at cryogenic temperatures, reaches a maximum near room temperature, and then decreases. Because D varies similarly for glasses and crystals (Figure 6), the difference between both kinds of phases for k necessarily results from the relative magnitudes and changes in C_p and D with temperature. For glasses, C_p overwhelms D , so the temperature response of k largely follows that of C_p . For crystals, the strong increase in C_p initially dominates at low temperature, whereas the continuing decrease in D prevails at high temperature, so the complex temperature response of k is due to the interplay of D and C_p . This difference has been the focus of both experimental and theoretical research, in which glasses are treated differently than crystals, e.g. [1].

Low-temperature methods involve little radiative transfer, and they can be corrected for contact resistance losses through comparison with LFA data (Figure 4). For silica, a small correction term of a few percent was used to merge data on D and k from a few K to the liquidus temperature [10].

For glasses, fits may be made to the LFA data with expressions of the form

$$D = FT^{-G} + HT, \quad (15)$$

(Figure 7). All data obtained so far are well described by Eq. (15) [18]. From phonon scattering models, the exponent G is expected to be unity for well-ordered crystals. However, for highly disordered feldspar crystals, similar fits give a small value for G of about 0.5. The transport properties of these materials are similar to those of glasses (see Pohl [1] for discussion), as borne out by the G values of 0.15–0.5 that we found for our glasses (Table 2), which are by definition highly disordered.

4.2 Effects of the Glass Transition and Melt Properties

All LFA studies of glasses have found that D decreases across the glass transition (Figures 5–7). These measurements probe relaxed melts, starting at temperatures corresponding to a viscosity of $\sim 2 \times 10^8$ Pa·s. One can interpret this value by considering the relaxation time-scale (τ_r) calculated from the Maxwell relationship ($\eta = G_\infty \tau_r$). Because the shear modulus at infinite frequency G_∞ is about 10 GPa, τ_r is ~ 1 to 10 ms, a value that is commensurate with the duration of the laser pulse in LFA. Consequently the glass transition in LFA heat-transfer experiments ($T_{g,LFA}$) occurs at a substantially higher temperature and lower viscosity than in viscometry experiments ($T_{g,12}$) simply because of the short time-scale over which the laser probes the sample. Above $T_{g,12}$, but below $T_{g,LFA}$, a viscous liquid appears frozen (glassy) on the short timescale of the laser pulse, although it can still flow over the longer (minutes to hours) timescale of a viscosity measurement. Although the state immediately above the glass transition is (metastable) supercooled liquid, the thermal diffusivity measured above $T_{g,LFA}$ represents that of structurally relaxed liquid up to and including superliquidus conditions and is denoted D_{melt} . For brevity, we refer to this state simply as melt or liquid.

Upon crossing the glass transition, D decreases substantially, to ~ 0.35 mm²/s for Ca-rich melts, but only weakly, to ~ 0.52 mm²/s for Al-rich melts (Figure 7; Table 2). The magnitude of the decrease in D at $T_{g,12}$ correlates with the melt fragility and also with the configurational heat capacity [11]. The close correspondence between C_p and D^{-1} is consistent with greater configurational changes in the melts producing greater disruption of lattice heat transfer [10, 11]. Increased disorder causes D to decrease because disorder is associated with a greater number of vibrational states, leading to an increase in the number of types of phonon collisions, and because enhanced collisions provide a shorter mean free path.

All LFA measurements indicate that melts have low D (Figures 3, 5–7, and 9), which depends on composition. For example, more polymerized aluminosilicates have higher D than less polymerized soda-lime glasses or slags [5, 11, 15].

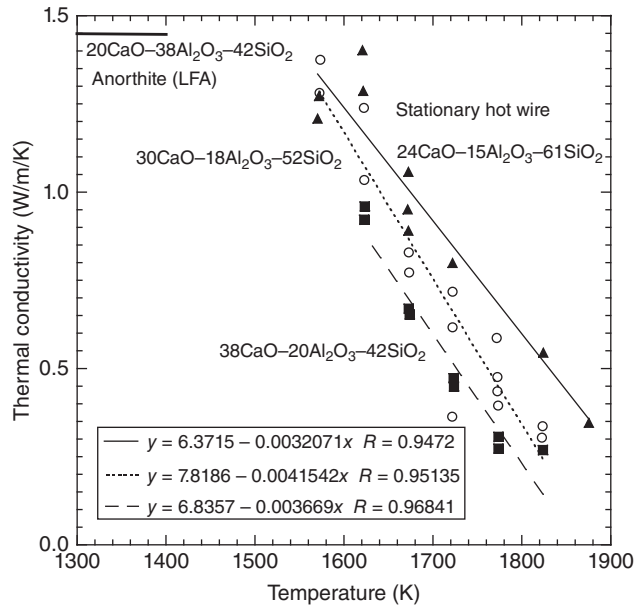


Figure 9 Thermal conductivity of molten slags (calcium aluminum silicates with varying proportions: labels are in wt %). Heavy solid line: LFA data on anorthite above the liquidus [11]. Symbols: examples of the many slags studied by Kang and Morita [15]. Lines are least squares linear fits. We do not provide details on compositions or fits in the tables because the T -dependence does not agree with LFA or thermoreflectance data (see text).

Data collected with contact methods on calcium aluminosilicate slags show a strong decrease in k with increasing temperature (Figure 9). This contrasts with the results of LFA or thermoreflectance studies, which suggest that D of the melt slightly increases with temperature (Figure 3; Table 2). The calculated k values of the melt (Table 3) consequently show weak changes (which themselves depend on the temperature dependence of heat capacity). The trend in D with T of the slags [15] cannot be due to radiative transfer, because this would artificially elevate k . This comparison points to the difficulty of accurately measuring thermal transport for melts and slags [5] and emphasizes the need for benchmarking the various techniques, with identical samples, especially at high temperatures.

4.3 Effects of Composition and Crystallinity and Correlation with Fragility

Mass and heat transport properties are linked to chemical composition such that a dichotomy exists between the properties of mafic melts (which have low degrees of polymerization and are referred to as basic in the slag literature) and of felsic (highly polymerized) melts, the latter having higher viscosity and higher thermal diffusivity. Strong correlations have been found with Ca and Al

contents, whereby increasing concentrations of either cation lowers D [11] (see Table 2). However, high Ca contents result in low D for glasses and melts, whether or not Al is present. Thermal conductivity of Ca–Al–Si molten slags varies in the same manner [15] (see also Figure 9). Similar responses exist for k and D because heat capacity and density of melts are approximately constant at high T and vary little over the small temperature intervals accessed in the heat-transfer experiments (spreads of 200–300 K exist in those of Kang and Morita [15]). These findings are consistent with the network-modifying role of Ca, which leads to an increase of NBO/ T as Ca increases [7, 11]. Calcium is also known to increase thermal expansivity of melts (Chapter 3.5), and D is connected with thermal expansivity for SiO_2 glasses [10]. For slags, k depends on NBO/ T [5].

Few data exist on the effect of Fe substitution on D values, although small amounts apparently decrease D for glasses at low temperature, which is consistent with Fe being a network modifier. However, at high temperature, iron cations act in a different way: in their presence, D of both glass and liquid increases as temperature increases, as discussed further in Section 4.4.

Interestingly, k for glasses at 298 K can be predicted from partial molar sums of oxides [7]. This situation is attributable to the slight compositional dependence of D in glasses (Table 2), whereas C_p is well predicted from oxide sums (Chapter 3.6).

Configurational changes in the liquid upon heating are reflected in the melt fragility, which describes how steeply viscosity decreases above the glass transition (Chapter 4.1). The nominal degree of polymerization (NBO/ T) is less useful as a discriminant because feldspathic melts are nominally fully polymerized, yet they show a range in D depending on whether they are Ca, Na, or K rich. Generally, both D of glass and melt decrease as fragility increases (Figure 10). Other factors must also be important, as indicated by the observed spread in values. Nevertheless, this well-defined trend substantiates that a link exists between heat and mass transport properties.

Density reflects both structural and chemical characteristics. The overall decrease in D_{melt} as melt density increases (Figure 11) is connected with the presence of heavy cations. Cations such as Ca and Fe have low-energy vibrations that are less effective at transporting heat. This effect is seen with glasses and crystals as well. Silicic melts typically have high D and η and low fragility and ρ , linking heat and mass transport. Similarly, k of glass has been linearly correlated with density for simple compositional series [7]. However, the linear dependence of k on ρ for glass does not hold over a broad compositional range [7]. Trends in k ascertained from direct measurements are more difficult to establish because of experimental

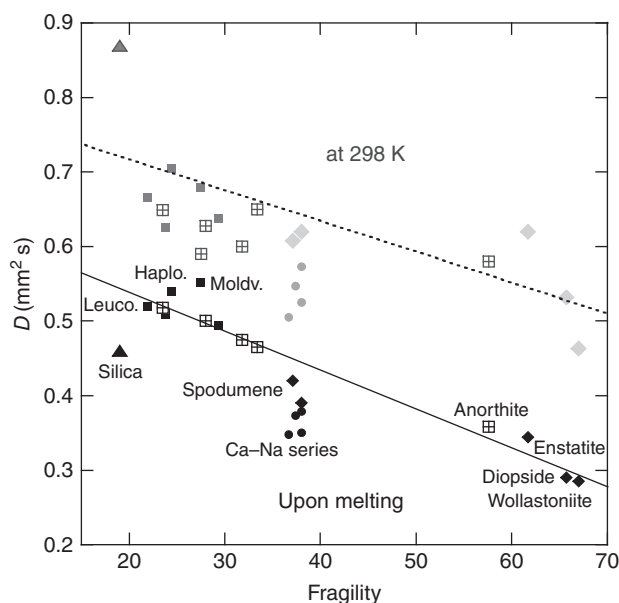


Figure 10 Correlation between thermal diffusivity and melt fragility. Symbols for liquid are as labeled. For glass, the same symbols are used but are gray. Lines are not fits but indicate ranges of values. Source: Data from [11, 17, and references therein].

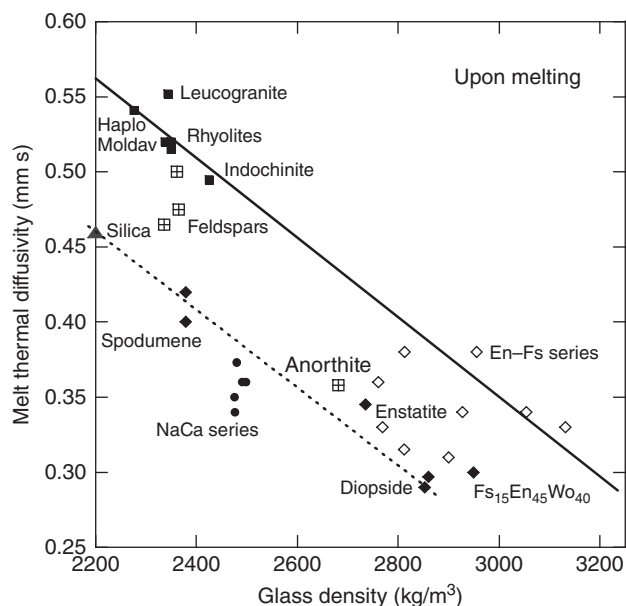


Figure 11 Dependence of thermal diffusivity of liquids on density at room temperature. Symbols and data sources as in Figure 10.

uncertainties as well as because of the possible presence of bubbles, strain, and crystallites.

For natural rhyolite samples, roughly parallel trends exist in $k(T)$ for different amounts of crystals (Figure 8). Because scatter exists in the data, we approximate the effect of a small amount of crystals as $k_{\text{sample}} = k_{\text{remelt}}F$,

where k_{remelt} is taken from Table 3 and F is related to the crystal fraction X by $F = 1 + 0.071 X$.

4.4 An Additional Mechanism for Heat Transfer?

The decrease in thermal diffusivity of crystals near room temperature with increasing temperature has long been attributed to phonon scattering; the same response of D with T in glasses suggests that a similar mechanism operates. Above ~ 500 K, spurious increases in thermal diffusivity have been observed as a result of ballistic radiative transfer between the heater and thermocouple, which does not actually involve the sample. In LFA measurements, this unwanted ballistic radiative transfer has been removed at all temperatures, yet slight upturns in D are still observed for some types of silica [10] and for Fe- and Al-rich glasses and their melts (Figure 7). Data fitting suggests that positive linear coefficients exist for the other samples, although the slopes are poorly constrained [11]. These data show a correlation between the strength of the upturns and Fe^{2+} content and/or charge transfer between Fe^{2+} and Fe^{3+} for samples with low total Fe content. The picture at high total Fe is more complicated [16].

It is possible that some of the increase in D observed in glasses at high temperature may be due to the removal of defects by annealing. For melts, some of the increase could be due to flow of the sample within the experimental apparatus because very thin plates can sag under their own weight near the glass transition temperature [10].

Whether the increase in D with T could result from increased disorder with T is not yet clear. The heat capacity and D^{-1} depend similarly on temperature [10], so D drops, whereas C_p increases across the glass transition, both changes being a response to increasing disorder from glass to melt. Available data suggest that high-temperature heat capacities of most silicate liquids are constant or increase with temperature (Chapter 3.6). However, few thermal transport data are available on the same substances. Additional measurements at high temperature of both thermal diffusivity and heat capacity are needed for a complete understanding of the high-temperature increases.

One clue for the origins of the upturns is a positive correlation of the cT term in Eq. (14) with Fe^{2+} content, for low total Fe, suggesting a radiative process since electronic and vibronic transitions are linked [11]. However, in $(\text{Mg}, \text{Fe})\text{SiO}_3$ glasses, the effect is reduced for high Fe contents, whereas it is enhanced if Ca is present [17]. More measurements are thus needed to understand the origin of the diverse upturns in D at high T . Hofmeister [4] provides an explanation based on radiative diffusion

and the recent discovery that D of glasses and crystals depends strongly on sample length, if this is below ~ 1 mm.

5 Perspectives

The next decade will see measurements of technologically important materials such as metallic glasses (Chapter 7.10) and of glasses in the form of fibers (Chapter 9.3) and thin coatings (Chapter 6.8). Owing to the conflicting nature of available data, especially at high temperatures, however, an urgent need exists for improved accuracy and for benchmarking with identical glass samples to minimize complications possibly caused by internal strain and crystallites. Identical thickness must also be used, because vibrational overtones diffuse heat only for thick samples, whereas fundamentals participate at all thicknesses, and the proportions of the two mechanisms change with thickness for silica glass and crystalline solids as well [4]. The importance of thickness is implicit in Fourier's Eq. (4) but has been overlooked because of large experimental uncertainties in conventional, contact measurements. Contact-free techniques will be developed, or existing methods will be improved (e.g. to remove ballistic radiative effects from three-layer models). However, the current focus in method development is the study of thin films, for which only the fundamental vibrations diffuse heat. These methods have been benchmarked against data on thick samples and particularly metals, so the considerable uncertainties and the effect of ballistic transfer on insulators (e.g. oxide glasses) in the most modern techniques have gone unrecognized. We are particularly concerned with the accuracy of methods such as thermorefectance, which do not measure heat transfer over a well-defined distance, but instead involve extensive modeling of the signal. Fourier's equations require that the distance be known; otherwise the results involve tradeoffs.

Because heat capacity and density are central to determinations of D and k as well as to relating these transport properties, reliable data are needed on the thermodynamic properties as well, especially at high temperatures, for the materials of interest. Accurate thermal expansivity data on the materials of interest is needed to establish slight changes in thickness as temperature increases, which affect both k and D in any measurement. This is particularly important upon melting, where improvements in methods are most needed and are most relevant to glassmaking and understanding magmatic processes and environments. Accurate heat capacity data are needed because this is a weighting factor when multiple mechanisms, multiple carriers, or parallel heat flow configurations are involved [4].

Once accuracy is established, data from many laboratories can be used to establish firm correlations of k and D with chemical composition and related variables such as fragility and, most importantly, to determine precisely the dependence of D and k on temperature and length. Once these goals are met, improvements in theoretical models will certainly follow. A promising model is the radiative diffusion model of [4], which with one parameter provides a reasonable estimate for the complicated dependence of k on T from absolute zero to ~ 1000 K. Three parameters are needed for high temperatures due to the small size of H in Eq. (15). To test this model, spectroscopic data are needed on the same materials studied in transport experiments. For glasses, this involves cryogenic conditions for both infrared spectra and measurements of transport properties. For melts, higher temperature spectra are needed. This model is general and so addresses radiative transfer in magma chambers and large vats of glass, which involves diffusion of high-frequency light. This type of heat transfer cannot be measured in the laboratory, where conditions are optically thin in the near-IR and visible, and so testing the model at conditions where comparison with measurements is possible will ascertain whether the formulation of [4] is correct and can be applied with confidence to conditions unattainable in the laboratory.

Acknowledgments

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List of Mathematical Symbols and Functions

a	absorbance
A	absorption coefficient
c	speed of light
C_p	heat capacity
D	thermal diffusivity
F	heat flux
h	Planck's constant
I	intensity
k	thermal conductivity
k_B	Boltzmann's constant
L	length scale
n	index of refraction
N	number of atoms in formula unit
P	pressure
Q	heat source
r_{th}	thermal resistance
t	time

T	temperature
u	velocity or sound speed
x, y, z	directional variables
Λ	mean free path
ν	frequency
ρ	density
σ	Stefan–Boltzmann constant
τ	mean free lifetime or characteristic timescale
ω	angular frequency

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4.6

Atomistic Simulations of Transport Properties

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1 Introduction

To begin with viscosity (Chapter 4.1) and ionic mobility (Chapters 4.2–4.4), transport properties are key parameters governing the kinetics of all processes involving glass-forming liquids, either industrially or naturally. Of course, much experimental and theoretical work has been devoted to these properties, but interpretations of the results are not necessarily unequivocal in terms of the basic mechanisms at play. In melts, the dynamics follow near the glass transition, a complex but universal frequency dependence whose origin has, for example, long been debated [1–3]. And it is probably superfluous to emphasize that viscosity is intimately connected to the fundamental problem of the glass transition (Chapter 3.2), which has not yet been solved in a general way.

As a complement to other kinds of approaches, atomistic simulations are useful to understand better transport properties of glasses and glass-forming liquids. Given the rather large number of atoms and long timescales to be considered to obtain insightful results, however, first-principles molecular dynamics (MD) calculations (Chapter 2.9) cannot be performed yet for this purpose, so this chapter will be restricted to classical MD simulations (Chapter 2.8). These are actually a useful technique to investigate the dynamics of atoms subjected to the classical laws of motion since the motion of atoms or ions can be tracked either individually or collectively to characterize it with the required detail as a function of time.

Owing to their fundamental importance, interatomic potentials used in MD simulations of transport properties will first be reviewed briefly. Relying mainly on the rest of the chapter on simulations made for lithium silicates, we will then introduce the concept of mean-squared

displacements (MSD) of ions as a function of time concerning reference positions. From the MSDs and related functions, one not only can distinguish time regions where the particles either move in cages, like in a crystal, or follow the diffusive regime typical of liquids but also can calculate transport properties such as the ionic conductivity or viscosity. How the coexistence of slow and fast ion motion gives rise to dynamical heterogeneities will then be discussed along the way to characterize them. Finally, insights on the mixed alkali effect will be presented and some features of the glass transition be discussed.

2 MD Simulations: Conditions and Potentials

Like MD methods, reverse Monte-Carlo simulations rely on the separability of the timescales of atomic and electronic motions to yield useful structural information (Chapter 2.8). They cannot produce directly particle trajectories, however, which is why classical MD with reliable interatomic potential is to be preferred for transport properties. In these simulations, practical constraints include not only system size and computing timescales (Chapter 2.8) but also the *strong* or *fragile* nature of the melts investigated, i.e. they depend on whether the dynamical properties are approximately Arrhenian or not (Chapter 4.1, [4]). The finite-size effects found for the former melts actually suggest that larger system sizes are required [5]. Besides, dynamical heterogeneities and the size of cooperatively moving regions of ions and atoms should be taken into account [3].

Of course, the adequacy of the selected interatomic potential to the problem investigated is of great importance. In addition, the choice of periodic boundary conditions must be checked since these can affect the

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cooperative motions of the mobile ions of the system as well as the network structure of the system. Particular attention must also be paid when slow dynamics are dealt with in glasses and supercooled liquids because the process can be considerably affected by rare events such as cooperative jumps of several ions. And another point to be mentioned is that the glass transition has usually been studied for binary melts because one-component systems were thought to crystallize readily. But this restriction is not necessarily serious if the system size is not too small [6], whereas these systems have in fact the important advantage of allowing rigorous theoretical treatments to be performed thanks to the validity of exact dynamic scaling laws.

For transport properties, the purpose of a simulation is not necessarily to reproduce faithfully the real system but, rather, to pinpoint the key structural or dynamical features at work. Likewise, the functional form of the potential and the precise values of its parameters are not critical for a most general phenomenon such as the glass transition. This is why relatively simple potentials such as soft-core (SC) or Lennard-Jones (LJ) potentials have been extensively used. The former is gaining importance because it is considered as a basis for understanding thermodynamic scaling. It consists of a repulsive, power-law term of the form

$$\varphi_{ij} = \varepsilon \left(\frac{\sigma}{r_{ij}} \right)^n, \quad (1)$$

where r_{ij} is the distance between particles i and j , whereas ε and σ determine the depth and size of the potential well, respectively. The hard-sphere model is the limiting case of Eq. (1) when n approaches infinity. As for the Lennard-Jones potential, its most general form is

$$\varphi(r) = \frac{E_0}{(q-p)} \left[p \left(\frac{r_0}{r} \right)^q - q \left(\frac{r_0}{r} \right)^p \right], \quad (2)$$

where E_0 is the depth of the potential well, r_0 the position of its minimum, and the parameters p and q have been given various values. The Lennard-Jones values with $p = 6$ and $q = 12$ have been extensively utilized in models of the glass transition (e.g. [7]). Variants of this model with the other values $p = 11$, $q = 12$ and $p = 5$, $q = 8$ have been selected to investigate the effect of the potential functions on the glass transition simulated for systems of different fragilities [8].

In dealing with specific properties of silicate and other ionic melts, however, recourse must be made to more realistic potentials. A Gilbert–Ida-type repulsive potential combined with Coulombic force has, for instance, been used successfully for silica and silicates [3]:

$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + f_0 (b_i + b_j) \exp \left(\frac{a_i + a_j - r_{ij}}{b_i + b_j} \right) - c_i c_j r_{ij}^{-6}, \quad (3)$$

where the first term on the right-hand side represents Coulombic interactions and r_{ij} designates interatomic distances (Å), a_i the ionic radius of atom i and b_i its softness parameter (also in Å), and f_0 a constant parameter ($=1$ kcal/mol/Å). As for the $c_i c_j$ parameters (kcal Å⁶/mol), they are introduced for correcting the curvature of pair interactions involving oxygen atoms. This potential has the advantage that each of its terms is additive not only for pair but also for atomic species, so it allows complex systems such as mixed alkali melts and glasses to be treated.

In this chapter, the potential used for lithium silicates is of the type (3) with parameters derived from *ab initio* MO calculations [9]. As a severe control of the quality of these parameters, the potential has been checked against the stability of lithium disilicate and metasilicate polymorphs at constant pressure. Even though it is not fully realistic, its quality is good enough for discussing dynamical mechanisms.

In ionic liquids, the inner structure of the ions must in addition be accounted for. An adequate potential often used for representing both the interaction among ions and interactions within each ion is of the form [3]

$$\begin{aligned} \varphi(R) = & \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{\text{eq}})^2 \\ & + \sum_{\text{dihedrals}} \frac{V_n}{2} (1 + \cos [n\varphi - \gamma]) \\ & + \sum_{i < j}^{\text{atoms}} \left(\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} \right) + \sum_{i < j}^{\text{atoms}} \left(\frac{q_i q_j}{\epsilon R_{ij}} \right). \end{aligned} \quad (4)$$

In Eq. (4) the first three terms describe bond, angle, and dihedral deformation energies, whereas the fourth represents a standard pairwise (6,12) Lennard-Jones potential and the last characterizes Coulombic interactions between atoms with charges q_i and q_j .

3 Dynamics

3.1 Mean-squared Displacements and Diffusion Coefficients

As a starting point in dynamical studies, one calculates the MSD of the positions of an ensemble of particles over time with respect to a set of reference positions. Whereas the MSD is restricted to the vibrational amplitudes in solids, in liquids, it increases continuously with time as a result of diffusive motion so that the transition from solid- to liquid-like displacements can be clearly distinguished. From the successive positions occupied by the particles considered, the MSDs are readily calculated with

$$\langle r^2(t) \rangle = \left\langle \left\{ \sum_{i=1}^N (r_i(t) - r_i(0))^2 \right\} / N \right\rangle, \quad (5)$$

where r is the displacement of particle i , be it an ion, an atom, or a molecule, N is the number of the species. As for the angled brackets, they represent in Eq. (5) an ensemble average for an equilibrium system or average for a long time for a glass or a quasi-equilibrated system exhibiting slow dynamics. In general, fast and slow motions of ions or atoms coexist with jumping or hopping between sites. To average out the resulting dynamical fluctuation is not necessarily easy when performing runs with different initial configurations because of the extremely large number of runs then required. Instead, it is better to average many time-series taken from a long run or some long runs along with time windows covering a wide range of initial times [3].

As a first example, the MSD of Li^+ in lithium metasilicate at 700 K, i.e. near the glass transition, can be divided into four regimes delineated by characteristic times (Figure 1a). Because $\langle r^2 \rangle \propto t^2$ at the shortest times, the motion is simply ballistic before the onset of a combination of vibrational and relaxation contributions is

observed. The vibrational contribution to the MSD becomes constant after ~ 1 ps. The MSD is nearly flat in this first interval, which owes its name of nearly constant loss (NCL) region to the near constancy of the dielectric loss. In time region II, some jumps to nearby sites are observed, so the MSD becomes nearly proportional to time. In the power-law region (III), the MSD is modified by the angle formed by the directions of two successive jumps before the diffusive region (IV) is finally attained at the time t_{dif} after which the MSD determines the elemental timescale of diffusion coefficients.

Diffusion coefficients are indeed the related important properties readily calculated. For a particle i , this coefficient is derived with the following Einstein equation from the MSD:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [r_i(t) - r_i(0)]^2 \rangle. \quad (6)$$

Given the finite timescales of MD runs, the calculation must of course be performed in the actual diffusive time region after t_{dif} .

Analogous time regions are found in MD simulations of 1-ethyl-3-methylimidazolium nitrate (EMIM- NO_3), an ionic liquid (Figure 1b) [3]. In this case, the relatively steep slope in the NCL region means that motions at short times have larger amplitudes, which is why the system can remain in the liquid state at much lower temperatures than for silicate systems.

Since atomic mobility of course decreases with decreasing temperatures (or with increasing pressure), the widths of the four time regions then become accordingly greater. At low temperature or under high pressure, region II may thus be erroneously regarded as a diffusive region, and the true diffusive region IV is no longer observed if it requires observation times longer than the timescale of the MD simulation. Conversely, long simulation times are required for studying slow dynamics.

Usually, the diffusion coefficients of ions depend on the rate at which the system that has been vitrified. Interestingly, the diffusion coefficients of Li^+ in rapidly quenched lithium silicate glasses are comparable with the experimental values [3, 10, 11] although experimental systems are usually more slowly cooled. This result thus suggests that, with respect to actual atomic rearrangements in macroscopic systems, the bias due to high cooling rates in MD simulations is compensated by other bias resulting from the small size of a simulated system subjected to periodic boundary conditions.

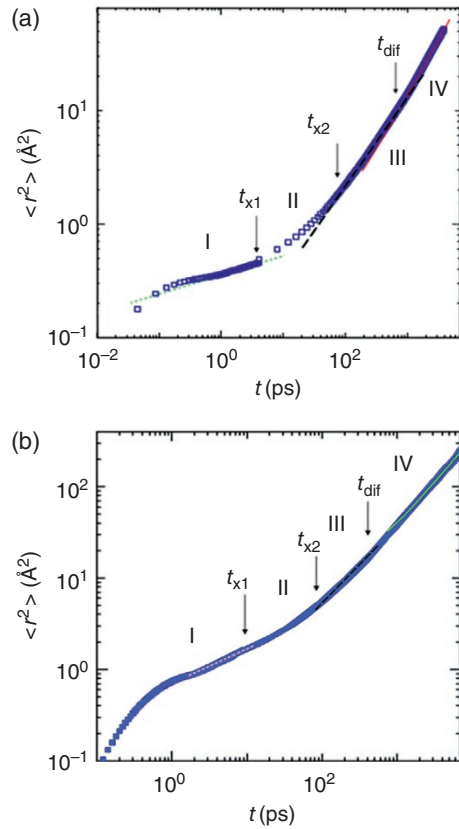


Figure 1 Time regions of mean-squared displacements as derived from MD simulations and delineated by the characteristic times t_{x1} , t_{x2} , and t_{dif} . Dotted line, power law in the NCL region; short dashed line, power law in region III. In Region II, MSD is nearly proportional to time. Solid line: linear dependence in region IV. (a) For Li^+ in lithium metasilicate glass at 700 K. (b) For EMIM^+ ion in the ionic liquid (EMIM- NO_3) at 400 K.

3.2 Temporal and Spatial Aspects of the Dynamics

In region III, the MSD of Li^+ ions in lithium silicates shows a power-law dependence when plotted against the cumulated number of jumps, whereas the cumulated

numbers of jumps follow a linear trend when plotted against time. Hence, the power law in region III originates in geometrical correlations between successive jumps. In a log–log plot, the change in the slope of MSD with decreasing temperatures then is caused by the complexity of the trajectories whose correlated back motions considerably contribute to the dynamical slowing down. The distribution of waiting times before jumps is generally another useful source of information on stochastic processes. For particle jumps, this waiting-time distribution shows a power-law tail at timescales comparable with the timescale of region III, so one might consider that it is at the origin of the power-law dependence of the MSD. This apparent discrepancy in the explanation of origins of the power law is caused by differences in the observation methods of the renewal jump processes. The reason is that the jumps of an ion to the next site and back to its original site are both counted in the analysis made for separating the temporal and spatial terms, whereas the returning ion is not counted in the calculation of the waiting-time distribution. Obviously, the time dependence of the MSD refers to the former situation. Thus the waiting-time distribution is not at the origin of the power-law time dependence of the MSD of ions. But the change in the waiting-time distribution nonetheless contributes to the slowing down of the dynamics through its effect on the mean jump rate at low temperatures.

3.3 Transport Properties

For a single-ion system, the ionic conductivity is related to the MSD of the ions by [12, 13]

$$\sigma^*(\omega) = -\omega^2 \frac{Nq^2}{6H_R kT} \int_0^\infty \langle r^2(t) \rangle e^{-i\omega t} dt, \quad (7)$$

where N is the number density of mobile ions, q the ion charge, k Boltzmann constant, T temperature, and H_R the Haven ratio (Chapter 4.2) between the tracer and bulk diffusivities, $H_R = D_t/D_b$. The D_t term in Eq. (7) is related to the geometrical correlations existing between two successive jumps of the ions from one site to another affected by other atoms and ions, whereas the D_b term is related to the collective property of all ions. Hence, the deviation of this ratio from unity is a measure of the cooperativity of their motions. The time dependence of H_R can also be evaluated [12] with

$$H_R(t) = \frac{\sum_i \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle}{\left\langle \sum_i \mathbf{v}_i(0) \cdot \sum_j \mathbf{v}_j(t) \right\rangle}, \quad (8)$$

where $\mathbf{v}$ is a velocity vector.

In equilibrium MD simulations the viscosity, η , can be directly calculated from the Green–Kubo relation [12, 14], which expresses transport properties in terms of the integrals of the autocorrelation functions of the off-diagonal components of the stress tensors. If needed, however, the viscosity can also be determined in nonequilibrium MD and reverse MD simulations. More simply, it is often derived from the diffusivity of atoms through the Stokes–Einstein relation (Chapter 4.3). Near the glass transition, however, deviations from this relation are often found, so a fractional power law can then provide a better description of dynamics over wide temperature ranges [1].

3.4 Space-time Correlations

The next step is to characterize the spatial and temporal distributions of pairs of particles in the system investigated. It is accomplished in terms of the van Hove function [15, 16], $G(\mathbf{r}, t)$, which expresses the probability of finding a particle j at a given positional vector $\mathbf{r}$ at a given time t , when the particle i was initially located at a reference point:

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)] \right\rangle, \quad (9)$$

Characterizing the structure and dynamics of the system, the van Hove function is a Fourier transform of a dynamic structure factor $S(\mathbf{k}, \omega)$ that depends on a wave number vector and a frequency variable. It can be split into self-part and distinct parts, the former and latter accounting for the cases $i = j$ and $i \neq j$, respectively. The self-part describes the motion of the initially marked particle at t for an observer whose eye is fixed on the initial position. It is defined as

$$G_s(\mathbf{r}, t) = (1/N) \sum_{i=1}^N \langle \delta(\mathbf{r}_i(t) - \mathbf{r}_i(0) - \mathbf{r}) \rangle, \quad (10)$$

where $\mathbf{r}$ designates a positional vector. In Figure 2, it has been calculated for various timescales for Li^+ ions at 700 K in lithium metasilicate for $r (=|\mathbf{r}|)$ and multiplied by $4\pi r^2$ so that the areas under the curves are proportional to the numbers of particles. If the function $G_s(r, t)$ obeys the Gaussian form, the solution of the diffusion equation will be [16, 17]

$$G_s(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp(-\mathbf{r}^2/4Dt). \quad (11)$$

For comparison, Gaussian functions yielding the same diffusion coefficient as the van Hove function are also shown. They are represented [3] by stable distributions with inverse exponential tails, $f(X) \sim |X|^{-1-\alpha}$, and

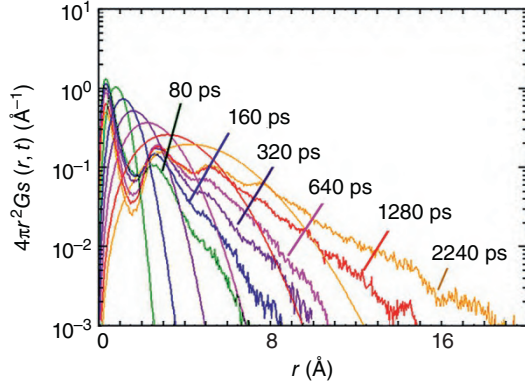


Figure 2 Self-part of the van Hove function of Li^+ ions in lithium metasilicate at 700 K: comparison of the MD simulated values for the indicated timescales with Gaussian dynamics (smooth curves) using Eq. (11), yielding the same diffusion coefficients. Both localized and delocalized ions exist.

exponential truncations. The exponent α is a Lévy index, $0 < \alpha < 2$ [18], which characterizes the form of the probability distribution the functional form being Gaussian when the value of α is 2. Clearly, one observes in Figure 2 heterogeneous (i.e. non-Gaussian) dynamics characterized by tails that extend farther when the time-scale increases. The deviation of the functional form from Gaussian implies the coexistence of fast and slow ions, which will be characterized later.

To understand mutual ionic motions, the distinct part of the van Hove function is calculated from

$$G_d^{\alpha,\beta}(\mathbf{r}, t) = (1/N_\alpha) \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \left\langle \delta(\mathbf{r} - \mathbf{r}_i^\alpha(0) + \mathbf{r}_j^\beta(t)) \right\rangle, \quad (12)$$

where N_α and N_β are the numbers of ions α and β , respectively, and the self-term $i = j$ is left out in the summations if $\alpha = \beta$.

If an ion β comes onto the site previously occupied by an ion α at the initial time t_0 , a new peak develops at around $r = 0$. Once normalized by the density, the function at $t = 0$ corresponds to the pair correlation function, $g(r)$.

The intermediate scattering function, which is a Fourier transform of the self-part of the van Hove function, can then be calculated with

$$F_s(k, t) = \left\langle \sum_{j=1}^N \exp \{ i\mathbf{k} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)) \} \right\rangle / N \quad (13)$$

where the $\mathbf{k}$ is the wave number vector difference before and after scattering. This function can be obtained from inelastic neutron scattering measurements (or related

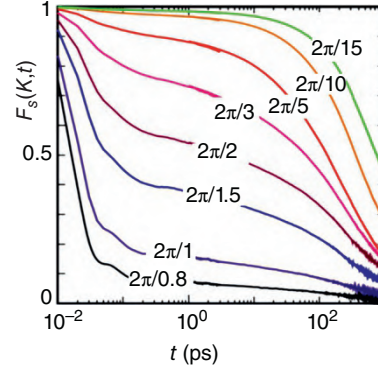


Figure 3 Intermediate scattering functions of Li^+ ions for the eight wave numbers indicated ($\text{\AA}^{-1}$) as a function of the MD simulation timescale in lithium metasilicate at 800 K.

ones). For Li^+ ions in lithium metasilicate at 800 K, it is a strong function of the wave number (Figure 3). It decays in several stages, which correspond to the time developments of MSD and van Hove functions. At the greatest wave numbers, the function accounts for short length-scale motion. It decays faster in the short time region, whereas at smaller wavenumbers (long length-scale motion) it shows a slower decay with a Kohlrausch stretched exponential form (Chapter 3.7),

$$\phi(t) = \exp \left[- (t/\tau)^\beta \right]. \quad (14)$$

The observed heterogeneous dynamics thus results from a combination of motions characterized by different length and timescales. A similar situation is found in other systems. In supercooled liquids, a fast β -process is observed at an early stage of the function, and it is then followed by slow α -relaxation [1].

4 Insights into Dynamic Heterogeneities

4.1 Slow and Fast Ion Motion

As exemplified in Figure 2, dynamics not described by Gaussian functions nor Brownian motion have been observed in many systems. Atoms or molecules in supercooled liquids, ions in ionically conducting glasses, and ionic liquids generally show such a dynamic *heterogeneity*, which actually originates from the coexistence of fast and slow atoms or ions. This frequent occurrence thus suggests the existence of underlying fundamental features common to these systems. Before looking for them, however, one needs a more precise definition of *fast* and *slow*. The definition can, in fact, be given in two complementary ways. In the first definition, one designates by *fast*

a dynamics accelerated by the forward correlated motions (or long jumps) and by *slow* dynamics retarded by ions with a localized motion and of a long waiting time between jumps. The second definition refers instead to decay rates, which are *fast* in short-time regions and *slow* in long-time regions involving diffusive motion with both accelerated and localized motions. In the following, we will use the first definition.

4.2 Characterization of Dynamical Heterogeneities

Jumps in supercooled liquids are readily visualized by MD simulations to give a detailed picture of ionic motion in terms of density maps where ion sites are defined by those positions that accumulate during the run. In a 2 ns ($\sim t_{\text{diff}}$) MD simulation of lithium disilicate at 500 K (Figure 4), one clearly distinguishes in this way isolated sites from extended channels through which diffusive motion of Li^+ ions takes place within the network of SiO_4 tetrahedra. In more detail, the displacements calculated in 1 ns

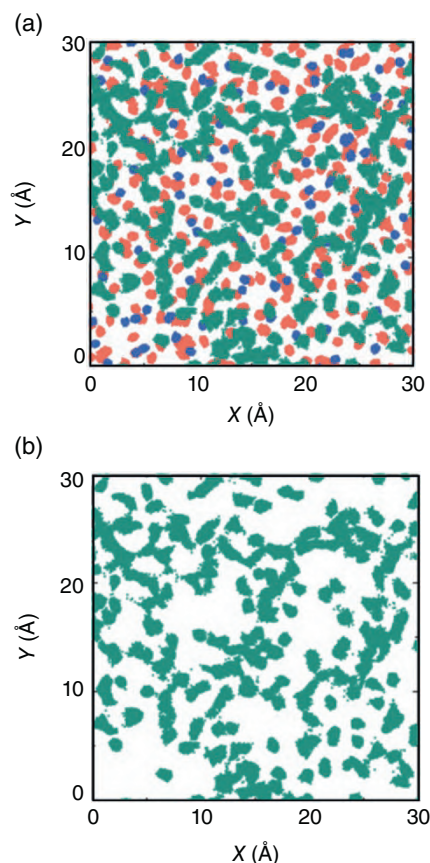


Figure 4 Atomic positions visited in a 6-Å slice of Li_2SiO_3 glass during a 2 ns run at 500 K. (a) Dark dots, Si and Li; light dots, O. (b) The same plot for Li^+ ions only, which contrasts sites either isolated or defining diffusion channels.

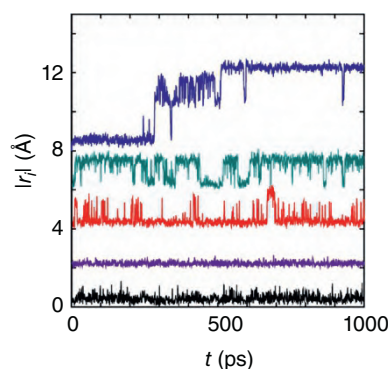


Figure 5 Absolute values of displacements at 500 K of five arbitrary chosen Li^+ ions. Initial values shifted upward to avoid overlaps.

for five arbitrarily selected ions clearly illustrate their dynamical heterogeneity (Figure 5). Two of these ions kept localized during the whole period. Two others underwent intermittent spike-like motion with an amplitude typically lower than 1.7 Å and a high back-correlation probability caused by site caging, which represented prejump motions found in the NCL region. Jumps were observed beyond a neighboring site for only one ion (Figure 5, top), which contributed to diffusive motion. Unsurprisingly, the longer and/or successive jumps contributing to diffusive motion are found more frequently at higher temperatures.

It is the decoupling between the timescales of the slow motion of network formers and the fast motion of mobile ions that results in the existence of recognizable ion channels in ionically conducting materials such as silicates. The structure of these ion channels (or jump paths) has long drawn the attention of researchers. Its importance in ionics has been well documented [3, 19, 20], so it is widely accepted. As an example, the fast motion of Li^+ ions in borate glasses has been related to the distribution of nonbridging oxygens [19] as expected from the built-in association of these oxygens with network-modifying cations.

4.3 Multifractal Analyses

As a matter of fact, large displacements tend to occur through cooperative jumps of several ions after time intervals that become shorter when the temperature increases. The very strong effects of temperature are clearly revealed by the marked contrast between the contour plots of Li^+ density maps calculated at 700 K and 1673 K for lithium metasilicate (Figure 6). The ion sites and paths are well recognized at 700 K: the dense zones represent long residence times on site involved in localized jumps, whereas the rarefied ones represent channels delineated by diffusive jump motion among shallow ion sites. At 1673 K, the distinction between these two kinds

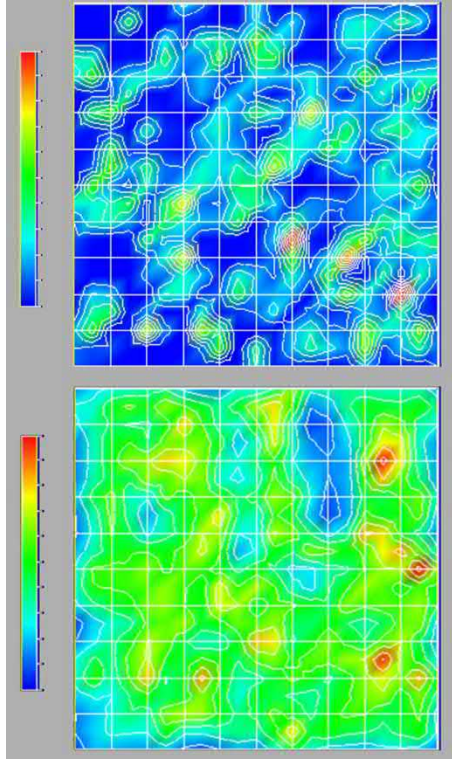


Figure 6 Spread of diffusive motion with increasing temperature in lithium metasilicate: a contrast between the contour plots of the density maps of Li^+ ions for 1 ns ($\sim 2 t_{\text{dif}}$) at 700 K (top) and for 400 ps ($\gg t_{\text{dif}}$) at 1673 K (bottom) as seen in an MD basic cell. Grids used for counting were 1/2 (for the length) of those shown in the figure. Program VENUS [21] was used for visualization.

of sites has nearly vanished as a result of a general spread of diffusive motion that leaves only a few remaining islands with relatively long residence time.

Such patterns of sites and paths are too complex to be characterized by a single fractal dimension, but they lend themselves to a multifractal analysis made in terms of singularity $[f(\alpha)]$ spectra [22] where the exponent $f(\alpha)$ represents the dimension of the part of the density profile that has a singularity of strength α . These spectra thus represent the distribution of structural dimensionalities and are, as such, useful measures of heterogeneities [22–24]. For Li^+ motion, temperature has an obvious effect on these spectra (Figure 7). Whereas their convex shape points to a multifractal character (mixing of exponents), their width decreases markedly with increasing temperatures as a result of increasing mixing of localized and diffusive motions of ions and, thus, of decreasing heterogeneities. Correlatively, the higher α -values at the highest temperatures indicate a larger spatial spreading and largest $f(\alpha)$ at the maximum means the largest capacity dimension (~ 3), which in this case is consistent with percolation of the ion channels during the timescale of the simulation.

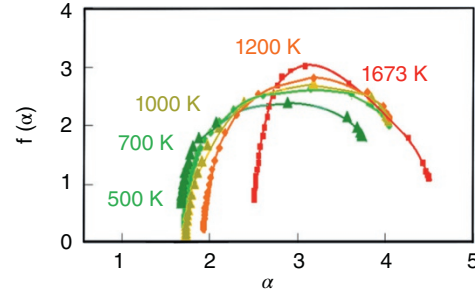


Figure 7 Singularity (multifractal) spectrum, $f(\alpha)$ for Li ions obtained from the density profile of Li ions during 1 ns at each temperature.

4.4 Non-Gaussian Dynamics

By definition, heterogeneities may be neglected if one is interested only in the mean dynamics of the system or if a *coarse-grained* MD simulation is performed whereby the system structure is simplified through a selection of its most salient aspects so as to reduce considerably the computing effort. In contrast, heterogeneities need to be considered to understand non-Gaussian dynamics at certain timescales, the non-Arrhenian temperature dependence of transport properties, or other nonlinear features such as the mixed alkali effect. Even in the former case, one should note that the mean value itself is affected by the heterogeneity of the dynamics.

Deviations from Gaussian dynamics are characterized by the following non-Gaussian parameter [16]:

$$\alpha_2(t) = (3/5) \langle r^4(t) \rangle / \langle r^2(t) \rangle^2 - 1. \quad (15)$$

which thus vanishes if the system obeys a Gaussian form. When evaluated at several temperatures for Li^+ ions [3], $\alpha_2(t)$ begins to be very small at short times, increases up to a maximum at around t_{x_2} , and then decreases slowly. In other words, α_2 increases until Li^+ ions jump out of their cages, and then it decreases as a result of the contribution of successive jumps with a large back-correlation probability.

The maximum value of α_2 , therefore, does not necessarily represent the largest heterogeneity. Hence, one may need to use other measures of heterogeneity such as the Lévy index, two cumulants [25], the variance, and the kurtosis of the distribution of the self-part of the van Hove function and multifractal spectra. From a physical point of view, convergence to a Gaussian form is expected through the exchange of slow and fast dynamics at longer timescales [26]. Consistent with this idea, Sokolov and his coworkers [27] have shown that the (power law) truncated Lévy flights slowly converge to a Gaussian form. For arbitrarily truncated Lévy flights, Vinogradov [25] has pointed out that the high-order cumulants vanish when the number of steps tends to be infinite so that the dynamics become Gaussian as well.

Before following Gaussian regimes, however, ions (or atoms, molecules) would spread considerably (Figure 2) to form multifractal structures (Figure 6) that differs from those of the Gaussian Dynamics [3].

5 Mixed Alkali Effect

The mixed alkali effect is characterized by strongly non-linear variations of transport properties when an alkali substitutes for another, for instance, by a minimum in viscosity [3] or by a maximum in electrical resistivity, whose origin has been extensively debated [28–36]. In MD simulations [30–32], an interesting inference drawn from the distinct part of van Hove functions has thus been the lack or decrease of jump motion between the different alkali-ion sites in mixed alkali glasses. The question has then been to determine how this existence of nearly distinct jump paths can account for the mixed alkali effect observed macroscopically.

For this purpose, consider the diffusivities of Li^+ and K^+ in mixed $(\text{Li}_{1-x}\text{K}_x)_2\text{SiO}_3$ at 700, 800, and 1673 K, which exhibit minimum values near the $x = 0.5$ in both glass and liquid states (Figure 8a). Interestingly, similar variations are calculated for the fractal dimensions of the random walks since the $2/d_w$ values of Li^+ ions decrease upon mixing with K^+ ions (Figure 8b) and vice versa. In addition, a change in the power-law exponent of the MSD is observed. Denoting by d_{w1} and d_{w2} the fractal dimensions of the random walk of the shorter (≤ 3 Å) and longer length scale (> 3 Å), respectively, one observes that the difference between d_{w1} and d_{w2} becomes smaller upon (Li, K) mixing, so it is related to the suppression of collective motions in the mixed systems. Finally, changes in paths upon mixing have also been found in density profiles [32] whose $f(\alpha)$ spectra indicate that the capacity dimension for the Li^+ path decreases upon mixing with K^+ (Figure 9). It has thus been concluded that the slowing down of the dynamics originates from the increase of the back-correlation probability of the motion within channels. This probability is itself related to the fractal dimensions of both random walks, d_w , and pathway, d_t [3, 31, 32]. The d_w value is a measure of the complexity of the trajectory that has a value of 2 when the motion is a free random walk.

A similar disruption of jump paths in the mixed $\text{Li}_x\text{Rb}_{1-x}\text{PO}_3$ has also been described from reverse Monte-Carlo simulations of structures made with the bond-valence technique [33]. Either from MD or Monte-Carlo simulations, there is a consensus on the role of the dimensionality of paths in the mixed alkali effect although some details depend on the assumptions used in each analysis.

There has in fact been a close relationship between experiments, theory, and simulation on this problem

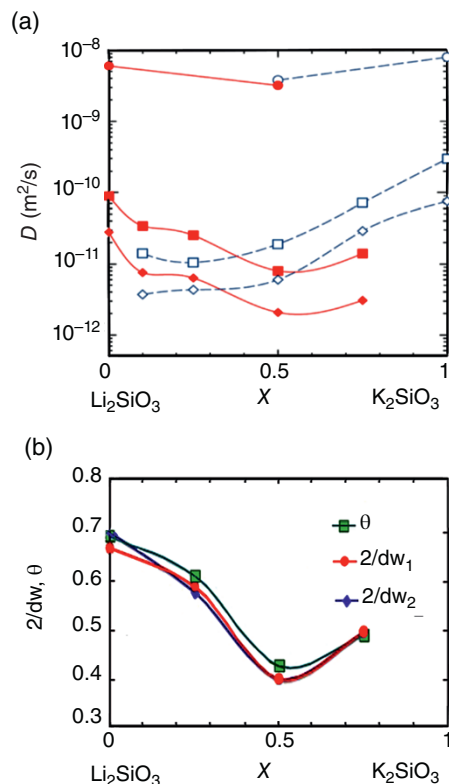


Figure 8 Mixed alkali effect for alkali diffusion in $(\text{Li}_{1-x}\text{K}_x)_2\text{SiO}_3$. (a) From top to bottom, diffusivities at 1673, 800, and 700 K as a function of x ; solid symbols, Li^+ ; open symbols, K^+ . (b) Changes in the reciprocal of the fractal dimension of the random walk, $2/d_w$, and in the power-law exponent of the MSD, θ at 700 K.

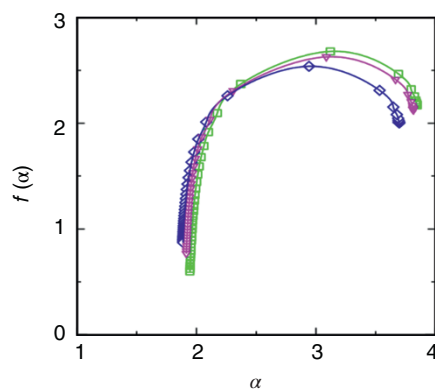


Figure 9 Mixed alkali effect for alkali diffusion in $(\text{Li}_{1-x}\text{K}_x)_2\text{SiO}_3$. Singularity spectrum of Li^+ ions obtained from 1 ns runs at 700 K for $x = 0$ (rectangles), 0.25 (triangles), and 0.5 (diamonds). Systematic decrease of the capacity dimension for the channel of Li^+ ions found with increasing of K^+ content.

[3, 28–36]. For example, Jain and Lu [36] have pointed out that the mixed alkali effect is not found in AC conductance at low temperatures, which is consistent with the results of MD simulations. Besides, the mechanism of confinement by fixed or pinned particles or walls

[3, 37] bears a definite similarity with the mixed alkali effect. When a randomly chosen small number of ions (or particles) are pinned down, the mobility of the majority of ions decreases concerning path changes. When ions in the wall of the basic MD cell are fixed, the intermediate scattering function indicates that the dynamics of the other ions gradually changes at a distance from the wall because the decay is slower and more stretched near it. In this case, the paths change only slightly for the majority of mobile particles, which means that the effect of the blockage propagates over a longer distance [1, 32].

6 Glass Transition and Thermodynamic Scaling

In addition to the glass transition temperature T_g , another characteristic temperature T_B has been identified in fragile liquids as a kink in the temperature dependence of relaxation times [3]. Recent MD work for ionic liquids has contributed to the understanding of this feature through the prediction of changes at the same T_B in the slopes of ion diffusivities, which can be observed in log–log plots. The simulated volume and partial potential energies for terms such as Coulombic, bonds, and angles of the system show inflections at both T_B and T_g , which correlate with changes in the geometrical freedom of the system. That is, a saturation of the number of fictive bonds (contact ion pairs) occurs near T_g , so the geometrical degree of freedom of the coordination polyhedra varies at T_B , in agreement with experimentally observed changes in the free volume of the system.

Complex variations of relaxation or transport coefficients in supercooled liquids, ionics in the glasses, and their dynamics are rather general and obey a thermodynamic scaling [3]. The validity of the scaling has been confirmed by MD simulations for some systems that include ionic liquids. Dynamical properties such as diffusion coefficients, D (or D/T), viscosity η , the timescale of α relaxation, τ_ω and some other physical properties are a function of the product ρ^γ/T , where ρ is the density of the system and T the temperature, i.e. the dynamics of many materials can be represented by a master curve characterized by the exponent γ of the density.

7 Perspectives

For MD simulations of slow dynamics near or below the glass transition temperature or of bigger or more complex systems including functional ones such as solid-state batteries (Chapter 9.5), the calculation speed may be expected to keep increasing as a result of further progress

in computation technology. Besides, coarse-grained modeling will be useful for systems possessing inner structures such as ionic liquids.

Different kinds of simulations will also be developed. Hyperdynamics with modified potential functions and/or temperature have, for instance, been introduced to search for free energy surfaces or rare events [38]. They seem to be useful, but some questions need to be clarified before applying them to supercooled liquids and glasses. How do modifications of the potential function affect the structure of the system and its long-time dynamics? Will they change the exponent connecting short- and long-time dynamics or not? If the applicability of such methods is established, then calculation costs will diminish considerably. With these developments, however, quantitative estimations of numerical errors for long runs and/or for hyperdynamics will remain necessary.

Thermodynamic and related entropy scaling should be tested for more systems, with respect to every species, to understand the general physics behind them. Using the thermodynamic scaling and/or related rules, one could then extend predictions of dynamics in a wider range of temperatures and pressures.

Finally, *ab initio* MD methods are promising approaches (Chapter 2.9) even though they are currently limited to small system sizes and short timescales because of calculation times 10^3 – 10^5 times longer than with classical methods. Without marked advances in computing power or methods, however, the difference will not be easily smeared out to make investigations of slow dynamics in current and/or more complex systems possible.

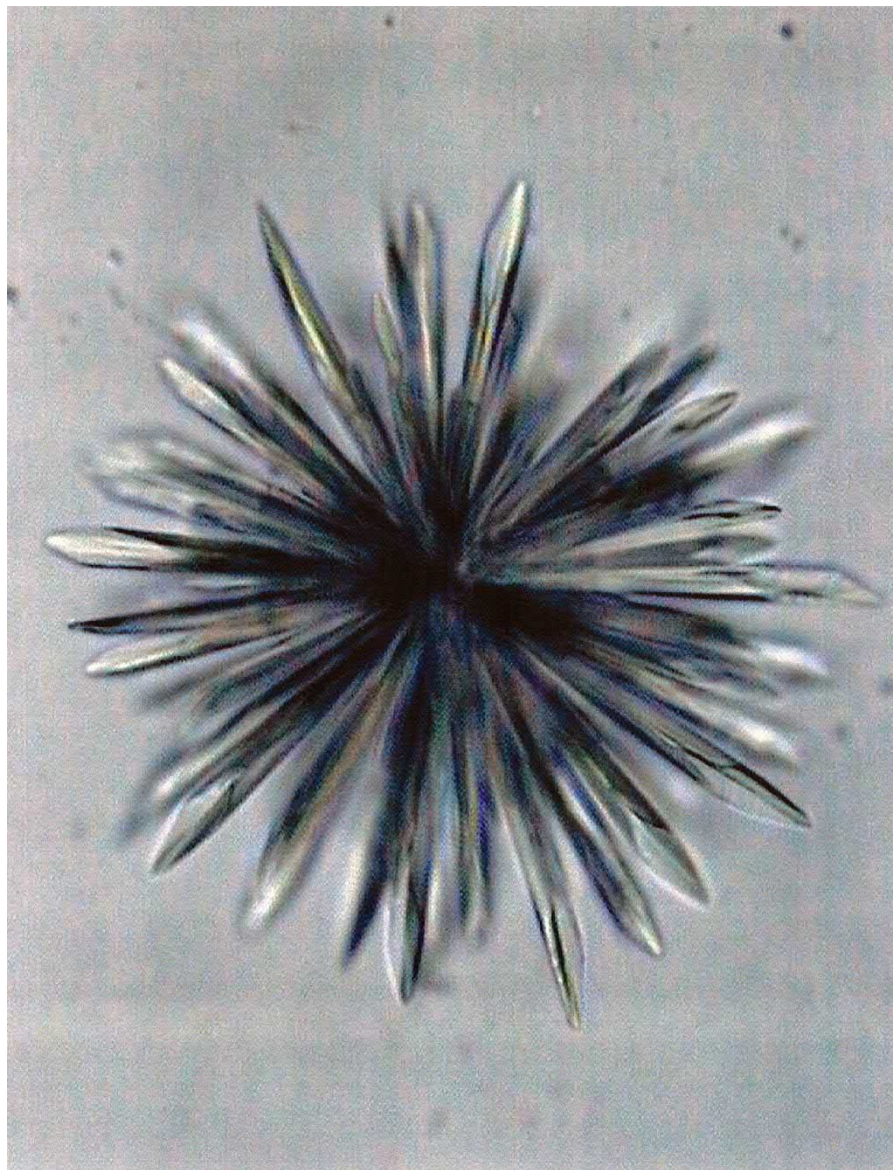
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Section V. Chemistry of Glass

Figure 1 Thermodynamics occasionally prevailing over kinetics in glassmaking: the precipitation of a 1 mm devitrite crystal [$\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$] in a plate of window glass. *Source:* Photo courtesy Hervé Arribart and Saint-Gobain Recherche.



With the exception of the coloring substances added, batches have been determined for most of the history of glassmaking by the raw materials locally available without any means to characterize them chemically. In the seventeenth century, the extensive incorporation of lead, for instance, leads to distinguishing *flint* and *crown* glasses from differences in density and refractive index and not from chemical analyses (Chapter 10.10). Because chemistry lagged considerably behind physics throughout the ages, the modern notion of chemical composition was defined only in the early nineteenth century when analytical methods made its determination possible. Hence, the birth of modern chemistry dates back to only two centuries ago when the relevant elements were identified and their specific effects on processes and properties began to be investigated.

In this fifth section, chemistry will be dealt with from two different standpoints: one will be the various ways in which chemical composition can be tailored for specific purposes and the other how temperature changes and interactions with the environment not only modify the chemical composition of glass but may also alter its original nature through phase changes. As a starting point, T. Bach, R. Haus, and S. Prinz present the most common methods currently used to analyze chemical compositions – which are generally very rapid and can be used for tiny samples; in addition they present the special analyses performed in industry for B, Li, and F and for glass defects as well as standard tests for determining resistance to chemical attack (Chapter 5.1). In the following chapter, I. Veksler reviews the main types of thermodynamic equilibria depicted by phase diagrams relevant to glassmaking and the general effects of the most common elements on their topologies; that these diagrams are most important tools in the design of new compositions is pointed out as they may, for example, directly indicate that attempts at decreasing viscosity would result in unwanted increases in liquidus temperatures (Chapter 5.2). To provide such fundamental information, phase diagrams were traditionally determined from time-consuming quenching experiments (Chapter 10.11). Thermodynamic modeling of phase equilibria thus represents an interesting alternative. Thanks to better input data and improvements in thermodynamic models and computing power, the different kinds of procedures reviewed by G. Ottonello now allow much information to be obtained rapidly and at a reduced cost, especially for new, chemically complex compositions for which the amount of experimental work to be done could be really substantial (Chapter 5.3).

Although vitrification is the general goal of the glassmaker, incipient crystallization is not always avoided (Figure 1) when it is not purposely triggered to synthesize glass ceramics (Chapters 7.11 and 8.5). The theories of crystal nucleation and growth, and the problems they

are still raising, are thus directly relevant to the glassmaker. They are reviewed by E. Zanotto, J.W.P. Schmelzer, and V.M. Fokin in relation to such other important features as the validity of the Stokes–Einstein–Eyring equation to describe the diffusion of elements required for growing a crystal (Chapter 5.4). Equilibria with gaseous phases must also be considered in industry, where the topic is directly relevant to fining, as well as in the earth sciences where volatile solubility increases so strongly with pressure that at water can become a major component of deep magmas. As described by B.O. Mysen, volatiles dissolve as either reactive or nonreactive species, which, depending on temperature and composition, can affect properties and structure at low concentrations: hydroxyl $[\text{OH}^-]$ and carbonate $[\text{CO}_3^{2-}]$ ions produced by solution of water and carbon dioxide cause, for example, network polymerization and depolymerization, respectively (Chapter 5.5).

Along with melting reactions within the batch, redox interactions of the glass components with the atmosphere or the tin bath in the float process (Chapter 1.4) are of great concern for the glassmaker, in particular with respect to color (Chapter 6.2). Redox reactions are of two kinds depending on whether the system may be considered *closed*, in which case the relevant length and time scales are small, or *open*, in which case the evolution is controlled by interactions with the environment. In both cases, the evolution of the system is determined by the chemical potentials of the relevant oxides under the temperature, pressure, and oxygen fugacity conditions of interest. These potentials can in principle be predicted from *Ellingham diagrams*, as explained by R.F. Cooper, but many reaction mechanisms may operate with different kinetics, so diffusion of oxygen to or from the melt is not necessarily the fastest. Competing mechanisms do exist, such as rapid diffusion of network modifiers toward the surface along with a counterflux of electron holes, whose relative importance varies with temperature in ways that do not necessarily lead to the lowest Gibbs free energy but ensure instead its most rapid decrease such that the systems may end up trapped in a metastable state (Chapter 5.6).

The acid–base properties of glasses are another extensively discussed topic because silicate melts have long been viewed as mixtures of *acidic* SiO_2 and *basic* metal oxides. Two difficulties must then be faced, however: first, these acid–base interactions are closely intermingled with redox reactions, and second, a thermodynamic acid–base scale analogous to pH cannot be designed for *associated* liquids lacking analogs of H^+ and OH^- ions, where it may even be problematic to know which oxide is the acid and which is the base. The concept of optical basicity was formulated to circumvent these difficulties and provide an a priori scale for dealing with these reactions. As defined by J. Duffy, this scale first relied on shifts

in the UV frequencies of Pb^{2+} and Tl^+ ions considered as probes of the Lewis electron donor character of oxygens determined by the overall cation environment and then refined in terms of a simple relationship with the density and index of refraction; also discussed are implications in terms of electronegativity and molecular orbital theory and applications to slags, borates, fluorides, or sulfides (Chapter 5.7).

Probably the first use made of chemical changes within the material came from the realization in 1909 that some glasses act as semipermeable membranes through which ions can be exchanged between two solutions. Predating shortly the concept of pH, this discovery of the *glass electrode* provided a means to determine acid–base titration curves from the variations of the emf measured between the solution of interest and a reference solution. From these early experiments described by A.A. Belyushtin and I.S. Ivanovskaya, the pathway to the modern pH meter was short; although the instrument can measure not only pH but also the activity of monovalent cations and redox potentials, its theory has not been fully worked out yet because of the basic problems raised by the complex nature of the hydrolysis/condensation reactions and interdiffusion phenomena occurring within the glass membrane and near the glass–solution interface (Chapter 5.8).

For any redox couple, the most fundamental parameters are the redox potential and its dependence on temperature and composition. For melts in which the ionic conductivity is high, the voltammetry experiments described by C. Rüssel allow these potentials to be determined along with oxygen activities and even diffusion coefficients of polyvalent ions; as for impedance spectroscopy measurements, they are especially useful for studying corrosion phenomena (Chapter 5.9).

Corrosion is an important practical issue because contact of hot glass with molds and fiberizing plates is, for

example, required in the production of containers and fiber glass. Under usual redox conditions, corrosion represents oxidation and dissolution of the metal by the glass. The first step in metal/glass interaction is wetting, followed or not by sticking, which is favored by oxidized metal surfaces. The important parameters determining these interactions are thus temperature, oxygen partial pressure, metal and melt compositions, redox potentials, and also the surface condition of the substrate. From their review of the mechanisms at play in these phenomena and of their dependence on metal composition, C. Petitjean et al. conclude that passivation of the metal surface by an oxide layer is desired for reducing corrosion; as actually observed for Cr- and Ni-bearing superalloys, however, the condition is that the oxide must have a very low solubility in the melt to ensure the stability of this layer (Chapter 5.10).

Finally, the celebrated chemical inertness of glass is not absolute. Water attack is a potential problem as soon as a glass piece has been fabricated, explained by M.-H. Chopinet et al. who describe the two fundamental types of ion exchange involved in *acidic* and *basic* weathering as well as the precautions to be taken to protect newly made flat and container glass from degradation (Chapter 5.11). Much more severe corrosion can take place over long periods as exemplified by the complete weathering of natural glasses in seawater (Chapter 7.3). A noteworthy feature is then the formation of a gel layer at the water–glass interface, which slows down markedly the rate of the reaction and is usually interpreted as a complex interdiffusion zone between the pristine glass and the corroding solution. However, the chemical analyses now made at a much higher spatial resolution presented by R. Hellmann point to more complex mechanisms involving instead coupled interfacial dissolution/precipitation reactions (Chapter 5.12).

5.1

Chemical Analyses and Characterization of Glass

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1 Introduction

During millennia glassmakers displayed considerable skill to distinguish empirically various kinds of raw materials and, thus, to ensure consistent production at a time when chemistry was basically nonexistent (Chapter 10.2). Real advances in glass technology have then paralleled and heavily relied on progress in chemical analysis (Chapter 10.11). It is, for instance, no coincidence that modern glassmaking began once alkali and alkaline earth elements were identified at the beginning of the nineteenth century. Likewise, innovation in optical glass at the end of the last century would have been impossible without knowing new elements such as barium or strontium and having accurate ways of analyzing them.

Diversity is in fact a hallmark of both man-made and natural glasses. Although the compositions of the former are generally not very complex, the variety of elements introduced to ensure specific properties is now so large as to require the feasibility of quick and accurate analyses for all of them. This situation holds especially true for highly optimized processes where compositional variations caused by apparently innocuous changes in raw materials can cause real fabrication problems (Chapter 1.2). As for natural glasses, whether formed on Earth (Chapter 7.2) or in the solar system (Chapter 7.1), they have generally more complicated compositions with about 10 *major* oxide components (i.e. with abundances greater than 1 wt %) whose proportions vary widely. Besides, the concentrations of many *trace* elements must also be known because they represent valuable sources of information on the origin and geological history of these glasses. They

are even relevant to archaeometry, as exemplified by the manner in which neolithic trade routes can be reconstructed from chemical analyses of obsidian artifacts (Chapter 10.1).

Hence, the goal of the present chapter is to review the most common methods currently used to analyze glass chemically and to describe which are most appropriate for major, minor, or specific elements. Analytically, the main steps involved in sample preparation and analysis are depicted in Figure 1 where the acronyms refer to the methods listed below. Some of them have already been briefly presented in the context of electron microscopy (Chapter 2.3), whereas many have a physical basis similar to those reviewed for determining glass structure (Chapter 2.2) because they also make use of rays emitted by the sample when subjected to an electromagnetic radiation or a beam of particles.

In structural studies, however, interest is primarily laid on spectral features pertaining to interatomic bonds, which are in contrast a nuisance in analyses of chemical compositions. In other words, in these analyses, the elements of interest must be probed with as little as possible interferences from their neighbors, which shift and broaden spectral bands (the so-called matrix effects). In practice, this goal is achieved at energies high enough to induce transitions between the electronic energy levels of inner orbitals. Element concentrations are then determined more or less directly from the recorded intensities of the transitions induced by X-rays, electron beams, or also very high temperatures.

Although a great variety of such spectroscopic methods have become available thanks to the small amounts of sample needed and their rapidity, automated nature, and thus reduced cost, the good old gravimetric methods will be mentioned first. Not only are they still used for characterizing the important glass property of acid, alkali, and hydraulic resistance, but they are in the last resort the only methods

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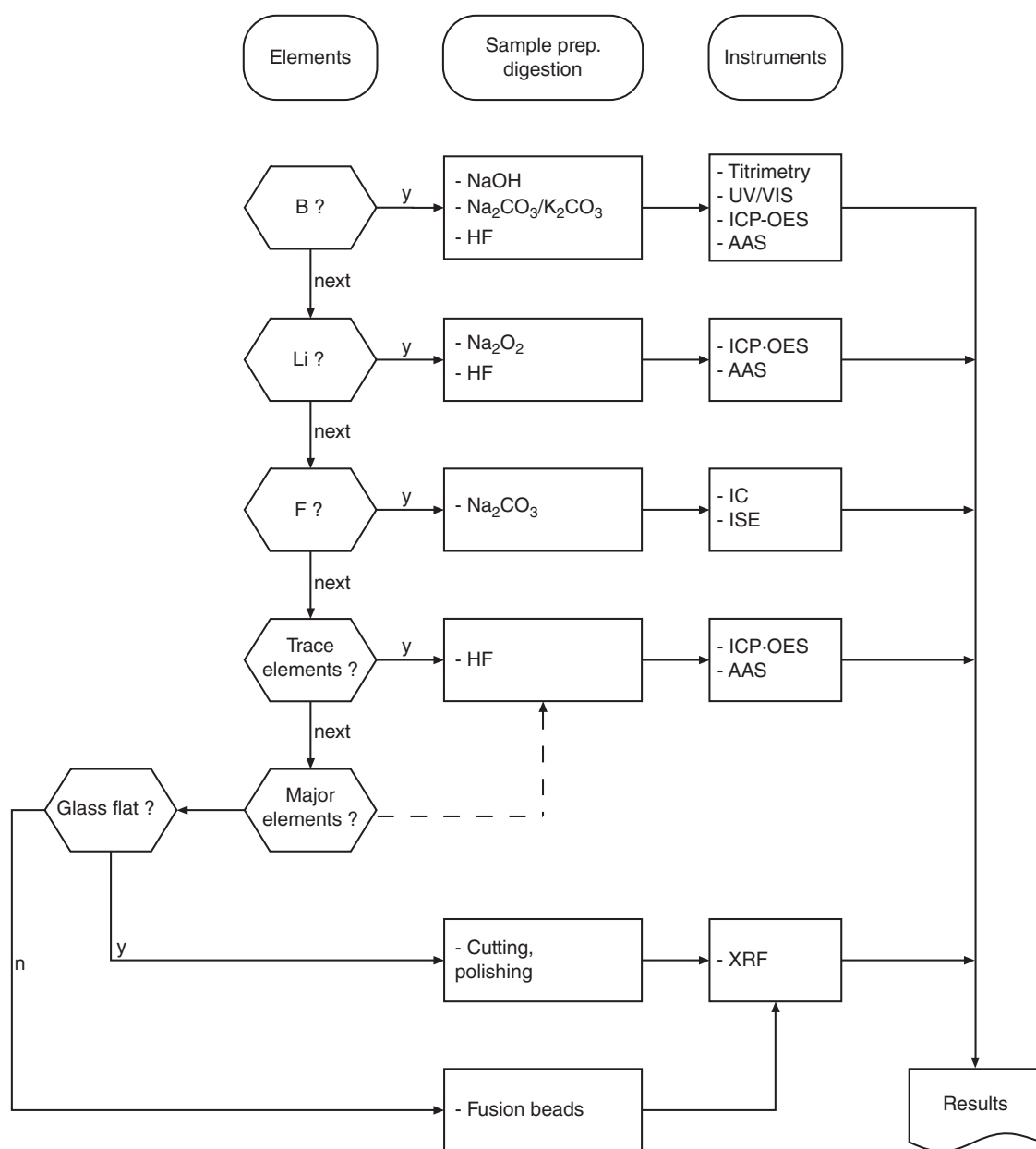


Figure 1 Flow chart for glass chemical analyses

yielding absolute results with a high accuracy, so they remain, directly or not, at the basis of the working standards required by modern methods. Attention will then be paid to X-ray fluorescence, inductively coupled plasma methods, atomic absorption spectroscopy, and electron microprobe analysis and secondary ion mass spectroscopy. Next the chapter will discuss the particular analytical problems raised by boron, lithium, fluorine, and iron. Finally, the chapter will conclude with determinations of the resistance to chemical attack and of glass defects.

List of Acronyms

AAS	atomic absorption spectroscopy
F-AAS	flame atomic absorption spectroscopy
HG-AAS	hydride generation atomic absorption spectroscopy
G-AAS	graphite atomic absorption spectroscopy
EDL	electrodeless discharge lamp
EPMA	electron probe microanalysis
ETV	electrothermal vaporization

HCL	hollow-cathode lamp
IC	ion chromatography
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
ISE	ion-selective electrode
LA	laser ablation
LIBS	laser-induced breakdown spectroscopy
SEM-EDS	scanning electron microscopy with energy-dispersive X-ray spectroscopy
SIMS	secondary ion mass spectrometry
XRF	X-ray fluorescence
WDXRF	wavelength-dispersive X-ray fluorescence
EDXRF	energy-dispersive X-ray fluorescence
μ-XRF	micro-X-ray fluorescence
UV-Vis	ultraviolet-visible spectrometry

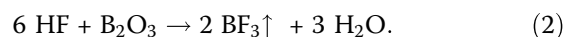
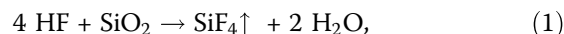
2 Gravimetry and Glass Digestion

As designed in the nineteenth century, gravimetric methods have long been the only ones available to determine chemical compositions. They rely on dissolution of samples in appropriate solvents followed by titration of the resulting solutions with adequate reagents under well-defined concentration or pH conditions and finally weighing of the dried precipitates obtained [1]. As early illustrated in the nineteenth century by determinations of atomic masses, their accuracy can be extreme because weights are the only quantities measured so readily with relative errors lower than 1 ppm.

For SiO₂ analyses, samples are, for instance, digested in Na₂CO₃, and the silica precipitated by addition of hydrochloric acid is then determined gravimetrically. In this case, however, concentrations are systematically underestimated because not all silica will precipitate, leaving a small portion of silicic acid in solution in the highly acidic range. The silicic acid in solution can be quantified by photometry. But these methods now suffer from their time- and labor-intensive nature – especially because a single element can be dealt with at a time – along with the big samples of the order of several grams required. These drawbacks have thus led them to be generally phased out by modern techniques.

As described below, they do remain used for a few elements and for the evaluation of mass loss through determination of acid and alkali resistance. Another reason why glass dissolution must be mentioned is that samples are still analyzed as solutions in a number of important

methods. Hydrofluoric acid (HF) is the only acid that readily dissolves oxide glasses. Digestion is performed either in a platinum crucible open to the atmosphere or, to minimize cross contamination, in a closed recipient, for instance, placed in a microwave oven where higher temperatures and pressures allow for shorter digestion times. As indicated by Eqs. (1) and (2), HF digestion of silicon and boron leads to formation of volatile SiF₄ and BF₃, which causes lower than expected findings in the analysis:



Trace amounts of boron can be captured in the solution with complexing agents. The remaining fluorides are evaporated at elevated temperatures by addition of high-boiling mineral acids such as H₂SO₄ or HClO₄. The presence of sulfuric acid prevents a dry substance from being obtained when HF is evaporated completely, whereas insoluble fluorides are transformed into sulfates. If CaO, PbO, or BaO is present in the glass, HClO₄ is required to avoid the formation of hardly soluble sulfates that could not be analyzed. For P₂O₅-bearing glasses, the phosphorus content can be underestimated because this element is a *fugitive* constituent at elevated temperatures.

3 X-Ray Fluorescence

3.1 General

For major elements, the main advantages of X-ray fluorescence (XRF) analysis are its high speed and reproducibility down to concentrations as low as 100 mg/kg or even less [2, 3]. In addition, XRF is well suited for glasses (Table 1) and represents one of the few methods capable of direct, accurate analyses up to 100 wt % without sample dissolution.

Upon interaction with X-rays of appropriate energies, an inner electron of an element is ejected and replaced, depending on atomic mass number, by another from a higher energy level of another inner shell (e.g. K_α transitions between K and L orbitals, K_β transitions between M and K, and L_α transitions between M and L). In all cases, these transitions give rise to an emission of X-rays whose wavelengths are generally lower than that of the exciting radiation. The wavelength λ (or frequency ν) of this XRF is characteristic of each atom. Because the frequency is simply related to the energy E emitted by the relationship $E = h\nu$ (h , Planck constant), it can be detected and recorded in two different ways as made in structure determinations (Chapter 2.2). In the first, the X-ray intensity is measured as a function of the frequency

Table 1 Reproducibility of XRF analyses (wt %).

XRF	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SiO ₂
Average value	0.504	0.0585	0.023	9.12	4.27	0.332	13.02	72.33
SD	0.005	0.0002	0.001	0.01	0.02	0.004	0.01	0.02
RSD	1.02	0.39	2.90	0.17	0.39	1.27	0.09	0.03

Average, standard deviation (SD), and relative standard deviations (RSD) for 10 analyses of a float glass sample.

(or wavelength $\lambda = c/\nu$, where c is the speed of light) after being diffracted by a crystal according to Bragg's law ($2d \sin \theta = n\lambda$, where d is the relevant interplanar spacing). In contrast to such *wavelength-dispersive* analyses (WDXRF), the X-ray intensity can alternatively be measured as a function of energy at a constant angle from the sample in *energy-dispersive* analyses (EDXRF). The former spectrometers can quantify elements from Na to U (wavelength 1–0.01 nm), whereas the latter do it from B to U (6.7–0.01 nm).

Sample preparation is the same in both cases. If the specimen has a planar surface, it has to be polished and reduced to the 40 mm size of the sample holder. Glass specimens must be freshly prepared to avoid glass corrosion, which would cause sodium depletion on the glass surface (Chapter 5.11). They are cut, milled, or polished and can be directly analyzed with regard to the main elements, no further sample preparation (digestion) being required. Measurements can be carried out within a few minutes with concentrations as low as 50 mg/kg depending on calibration standards. Alternatively the glass can be ground down to a grain size of about 100 μm , mixed with lithium tetraborate and melted at 1300 °C to yield a bead that can then be analyzed directly.

Usually approximately 20 certified reference standards are required for a careful cross-checked calibration.

3.2 Wavelength-Dispersive X-Ray Fluorescence

In wavelength-dispersive X-ray fluorescence (WDXRF) analyses, the fluorescence signal is diffracted according to Bragg's law by a single-crystal analyzer. Because the angle of incidence is fixed, different diffraction angles represent different wavelengths, which are recorded by a scintillation counter and a flow proportional counter. Today available WDXRF instruments have an additional semiconductor detector for analysis of major elements to shorten measurement times. Various diffracting crystals are used (e.g. LiF220; LiF200; Ge111), now including even organic ones (thallium acid phthalate [TLAP], pentaerythritol [PET]) and the so-called layered synthetic microstructures (LSMs), which are made up of alternating layers of elements of high and low atomic numbers. These

alternating layers of high- and low-density materials simulate atomic planes in crystalline materials and the spacing between them (LSM Ni/C) and are used for elements of the second period, ideally allowing the quantification of elements from boron to uranium. For light elements (B, C, N), XRF is easily absorbed by the sample itself, so the radiation emitted strongly depends on the glass surface and preparation method. Only in rare cases can boron be detected and determined in a reproducible manner. Boron and lithium are two elements that are not quantifiable by XRF, which is why lithium tetraborate can be used for preparing the analyzed beads. For fluorine and elements of higher atomic numbers, an increased reproducibility can in contrast be achieved, which makes WDXRF ideally suited for production control.

3.3 Energy-Dispersive X-Ray Fluorescence

In energy-dispersive X-ray fluorescence (EDXRF) the sample emits a secondary characteristic fluorescence radiation, which is analyzed by a semiconductor detector simultaneously discriminating and counting all photons by energy. Spectrometers can thus have a significantly more compact design than for WDXRF (cf. Chapter 10.1). A lower power X-ray tube is then used, however, so that fewer atoms are excited and the resolution is reduced because of more pronounced line overlap especially for the light elements Na, Mg, Al, and Si. In short, modern EDXRF instruments are capable of analyzing glass test specimen at high speed, but WDXRF is recommended instead if reliable analyses of both major and minor elements are needed (e.g. Na or Fe in silica sand).

4 Inductively Coupled Plasma Methods

4.1 General

Since its introduction in 1975 under the name of inductively coupled plasma atomic emission spectroscopy (ICP-AES), this method has gained wide acceptance [4]. The sample is digested, generally in an HF solution before the solution is nebulized into an argon stream that

transfers it into a plasma torch where it is dried immediately, atomized, ionized, and excited at temperatures up to 10,000 K. In a few seconds the electromagnetic radiation spontaneously emitted is analyzed from about 150 to 800 nm by one or several semiconductor CCD detectors. Because the spectrum also includes ion emission lines, the technique is now better termed inductively coupled plasma optical emission spectroscopy (ICP-OES). Alternatively, the atoms/ions formed can be transferred into a mass spectrometer for analysis. With inductively coupled plasma mass spectroscopy (ICP-MS) method, one can in addition discriminate isotopes of the same element from their mass differences.

Alternatively, glass samples can be investigated directly if the sample is vaporized via electrothermal vaporization (ETV), laser ablation (LA) with nano- or femtosecond pulses, or laser-induced breakdown spectroscopy (LIBS) (see below). Thanks to the high sensitivity of inductively coupled plasma (ICP), only tiny amounts of sample material have to be weighed out, which results in higher relative weighing errors and lower recoveries.

4.2 Inductively Coupled Plasma Optical Emission Spectrometry

The major advantages of the method are (i) a high sensitivity so that trace elements can be analyzed down to 0.1 mg/kg; (ii) analyses done very rapidly thanks to the simultaneous detection of all element lines at several wavelengths for each of them; (iii) internal standards used to correct fluctuations of plasma temperature, Ar stream, and viscosity; and (iv) high sample throughput (40 samples/h) when recording the entire spectrum. There are of course disadvantages: (i) digestion of solids (glass) is generally required, in which case Si and B analyses are not possible if HF is used because of element losses into the gas phase; (ii) dilution errors result in a considerably lower reproducibility for the main elements compared with XRF; (iii) the increased effort required for determinations of alkali elements because of the alkali effect described below; and (iv) considerably higher investment and operating cost than for competing methods such as F-AAS.

In modern glass analytics the widely used sequential ICP spectrometers with photomultiplier tubes are no longer used. In specialized laboratories Paschen–Runge spectrometers are preferred because a high spectral resolution is required, which does not allow for a compact design. Thanks to their lower production costs and compact design, echelle spectrometers are nowadays the most common ICP design [4].

Most ICP-OES spectrometers allow for both radial (side-in) and axial (end-on) measurement without modification of the instrument setup but at the expense of sensitivity. Purely radial or axial spectrometers do not

require optical mirrors and do not have losses in sensitivity. Some instruments offer the possibility to carry out axial or radial measurements by changes in torch setup. The quantification limit is ten times lower with an axial than a radial geometry since the detector captures ions along a greater optical pathway. On the other hand, the axial design leads to an increased perturbation of excitations, which results in a pronounced tendency for recombination of ionized alkali elements to alkali atoms (*the alkali effect*). If lithium is measured in the presence of sodium, an equilibrium state exists in the plasma between lithium atoms and ions. If a lithium atom emission line is selected for quantification and if a considerable amount of other alkali elements is present in the sample (e.g. Na), then these other alkalis are also ionized. By recombination of ions with electrons in the plasma, the equilibrium shifts toward Li atoms so that too high Li concentrations are obtained if a lithium atom emission line has been selected for calibration. On the other hand, the axial setup may lead to a deposition buildup, which affects the argon stream and reduces the lifetime of the torch.

In general ICP-OES is well suited for the determination of trace elements in glass because its limit of quantification is considerably lower than that of F-AAS. The same applies to the system that can be fitted to an ICP-OES for the separation of hydride-forming elements in the gas phase. Lower limits of quantification can be achieved thanks to an improved signal-to-noise ratio; typically, however, this is not required in glass analytics.

Owing to the analytical importance of both techniques, it is useful to compare the results obtained with XRF and ICP-OES for ten analyses of the same float glass (Tables 1 and 2). The relative standard deviations of the main elements are smaller with the former than with the latter. Deviations in Na₂O content are due to the alkali effect, which has not been corrected here because only the precision was of interest. For float glass, analyses must be performed on the “air” face except for tin for which the so-called tin count is of course determined on the tin side. Unfortunately this determination is not standardized. Because it depends on the choice of the excitation conditions, measurements made in different laboratories with different analytical equipment and instrument settings are not directly comparable.

4.3 Inductively Coupled Plasma Mass Spectroscopy

In a more sensitive method, the optical spectrometer of ICP-OES is replaced by a mass spectrometer whereby the ionized atoms are accelerated and deflected by magnetic and electric fields [5–7]. The ions are then discriminated according to their mass-to-charge ratio when they

Table 2 Reproducibility of ICP-OES analyses (wt %).

ICP-OES	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O
Average value	0.426	0.0520	0.017	8.92	4.40	0.249	12.04
SD	0.007	0.002	0.001	0.214	0.195	0.008	0.243
RSD	1.73	3.71	3.79	2.40	4.44	3.34	1.88

Average, standard deviation (SD), and relative standard deviations (RSD) for 10 analyses of the same float glass sample as in Table 1. Quantification of SiO₂ not possible because of HF digestion.

hit the collectors where the ion fluxes give rise to small electric currents that have to be considerably amplified to yield a mass spectrum. The limits of quantification are about one thousand times lower than for ICP-OES, but the much higher cost of the equipment markedly restricts its uses in industrial glass analytics. The main application is the monitoring of the boron content down to 0.05 mg/kg in the high-purity quartz used for the production of silica crucibles serving for growing Si crystals with the Czochralski method for the semiconductor industry.

In contrast, the unique capabilities of ICP-MS are extensively exploited in fundamental research. Work done on extraterrestrial and geological glasses (Chapters 7.1–7.3) is in particular taking advantage of the possibilities of analyzing tiny or highly spatially resolved parts of samples through LA and of measuring accurately even isotope compositions [8]. In these analyses problems are raised by different ionic species that have the same mass, e.g. ³⁸Ar¹H and ³⁹K. To eliminate such *isobaric* interferences, the so-called collision and reaction cells are used whereby ³⁸Ar¹H⁺ can, for instance, be split by collisions with hydrogen, leaving ³⁸Ar, which is then easily distinguished from ³⁹K.

5 Atomic Absorption Spectroscopy

The development of ICP-OES has restricted the use of atomic absorption spectroscopy (AAS) to determinations of trace concentrations of coloring (Ni, Cr, Mn, Co, Cu, V, Fe, Mo) or environmentally and food-relevant (Pb, Cd, Ba, As, Sb, etc.) elements as prescribed by industry standards. The apparatus consists of a high-temperature atomizer unit, an element-specific radiation source, and a detector [9]. The concentration of the element studied is determined from the intensity ratio between the primary beam (*I*₀) and the radiation measured for the sample (*I*), which is introduced as a solution, dried, and atomized.

High temperatures are obtained in the atomizer with the flame of a burner (F-AAS) or a graphite furnace (G-AAS) with which concentrations down to 1 mg/kg for F-AAS and 1 µg/kg for G-AAS can be measured,

respectively. In fact, F-AAS is more reliable than ICP-OES and is less affected by element interferences because it usually involves hollow-cathode lamps (HCL), which are element specific because they consist of a cathode in the form of a hollow cylinder containing the element of interest. A special form of the HCL is the electrodeless discharge lamp (EDL). This lamp has a high radiance and a low spectral linewidth. Thanks to lower detection limits, it is best suited for elements such as As, Se, and Te.

Either an acetylene/air (*T* = 2300 °C) or an acetylene/nitrous oxide mixture (*T* = 2700 °C) as fuel gas is used depending on the testing purpose. Almost all elements can be determined without interferences and at good sensitivity. An advantage of F-AAS is the possibility of determining alkalis in the emission mode because these elements emit characteristic lines when thermally excited. This feature will make the use of expensive HCL unnecessary. Contrary to ICP-OES the determination of characteristic emission lines takes place at considerably lower temperatures of 1500–2700 °C. This means that predominantly atomic emission lines are observed, which will not bias the analysis, whereas in ICP analysis both atomic and ionic emission lines occur, causing the aforementioned phenomenon of ionization interference.

The main drawback of all AAS methods is the sequential mode of measurement, which requires frequent lamp changes since simultaneous measurements are not possible with HC and ED lamps.

To avoid this limitation, a xenon short-arc lamp (Chapter 6.9), which is a continuously emitting light source, can be employed and makes it possible to cover the entire spectral range of AAS. The photomultiplier detector used in the AAS so far has been replaced by a CCD detector, which has been regularly employed in ICP-OES equipment for years. These detectors are not as sensitive as photomultipliers, but this disadvantage is more than compensated by the high radiation intensity of the xenon short-arc lamp. These two innovations allow for simultaneous detection of absorption spectra, which in turn result in an improved linearity and signal-to-noise ratio and lower limits of quantification. The background

noise of the CCD detector is of course not considered in the actual absorption measurement.

6 Microprobe Analyses

6.1 Electron Probe Microanalysis

With electron probe microanalysis (EPMA), also termed electron microprobe analysis (EMPA), the chemical composition of a sample is determined from the wavelengths and intensities of the X-rays emitted upon bombardment of its surface by electrons accelerated at energies typically ranging from 5 to 30 keV [10, 11]. The electrons are released from a glowing tungsten filament or some other source, accelerated under vacuum in an electric field toward the anode and focused by an electromagnetic system of lenses as a spot of a few microns onto the sample surface, which must be highly polished and usually coated with carbon or gold to prevent electrical charging. The element-specific X-ray photons emitted are then detected and analyzed with either an energy-dispersive (EDS) or a wavelength-dispersive (WDS) X-ray spectrometer as described above and in Chapter 2.3. The latter configuration compares favorably with standard scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) systems in terms of general sensitivity, spectral resolution, detector dead time, analysis of light elements, and risks of erroneous interpretation of qualitative spectra.

Although EPMA is a quick, fully quantitative method for all elements from B, it is not much used in industry where XRF is generally preferred. In addition to not being appropriate for analyzing trace elements, its drawbacks are the need of preparing highly polished, coated sample surfaces, of calibrating the instrument with appropriate standards to take into account specific matrix effects, and of adopting special procedures (low voltage and rastering of the electron beam on the sample) when analyzing alkalis and other elements prone to volatilization under the electron beam. But a major advantage is the visualization of the sample, which makes it possible to select a particular point of the surface for analysis. This is the reason why EPMA is extensively used in earth and materials sciences where detailed analyses of heterogeneous samples have to be routinely made. Although EPMA is in principle not sensitive to the redox state of an element, procedures have been designed to overcome the problem as made for iron in glasses [12].

6.2 Secondary Ion Mass Spectrometry

Alternatively, a sample surface can be bombarded by a focused beam of ions under a very high vacuum. Typically less than 1% of the atoms of the disorganized surface of the sample are then sputtered as *secondary ions* that

can be collected and analyzed with a high-resolution magnetic sector mass spectrometer, which thus discriminates between the various isotopes of a given element [13, 14]. Different instruments have been designed on this basis for specific applications. Primary ions such as Ar^+ , Xe^+ , Cs^+ , $^{16}\text{O}^-$, or $^{16}\text{O}_2^+$ are commonly used at energies in the 4–12 keV range, the particular one selected depending on factors such as the desired size of the primary ion beam, which ranges from 10 nm to 1 μm , and the nature of the sample investigated; oxygen and cesium ions are, for instance, recommended for analyzing electropositive and negative elements, respectively. Analyses as a function of penetration depth can also be performed with a resolution of 1 nm in the so-called dual-beam mode whereby the sample surface is continuously atomized with an ion beam (usually Cs^+) while a second ion beam is used to investigate the chemical composition of the newly created surface. This method does not always allow for a precise quantification, however, although quantitative results can be obtained by comparison with other samples.

As secondary ion mass spectrometry (SIMS) instruments are the most expensive analytical tools reviewed in this chapter, they are used only when a high spatial resolution is required for heterogeneous specimens or when the sample is too small to be analyzed by other methods as samples volumes as low as a few pg can be analyzed. The possibility of mapping chemical compositions is then especially valuable, as illustrated by a determination of the composition of a nonstoichiometric nepheline crystallizing as tiny dendrites at high degrees of supercooling in an aluminosilicate melt (Figure 2). Despite being the most abundant isotope of the most abundant element of this sample, ^{28}Si yielded in these analyses the lowest number of counts simply because of its low ionization efficiency under the primary $^{16}\text{O}^-$ ion beam used. For glasses, SIMS is in fact mainly the preserve of geo- and cosmochemistry especially since analyses can be made for a variety of volatile species such as H_2O or CO_2 [16] and for trace elements down to the ppm level as well as for determinations of isotope ratios [8]. In glass analytics, the technique is in contrast restricted to the investigation of surface defects by chemical analyses made on the first few atomic layers.

7 Special Elements

7.1 Boron

All other methods for boron analyses require sample digestion. By gravimetry, the ground sample is mixed with sodium hydroxide, melted above 600 °C, and quenched. The sample is partially dissolved in water, and the solution titrated with HCl against bromocresol purple

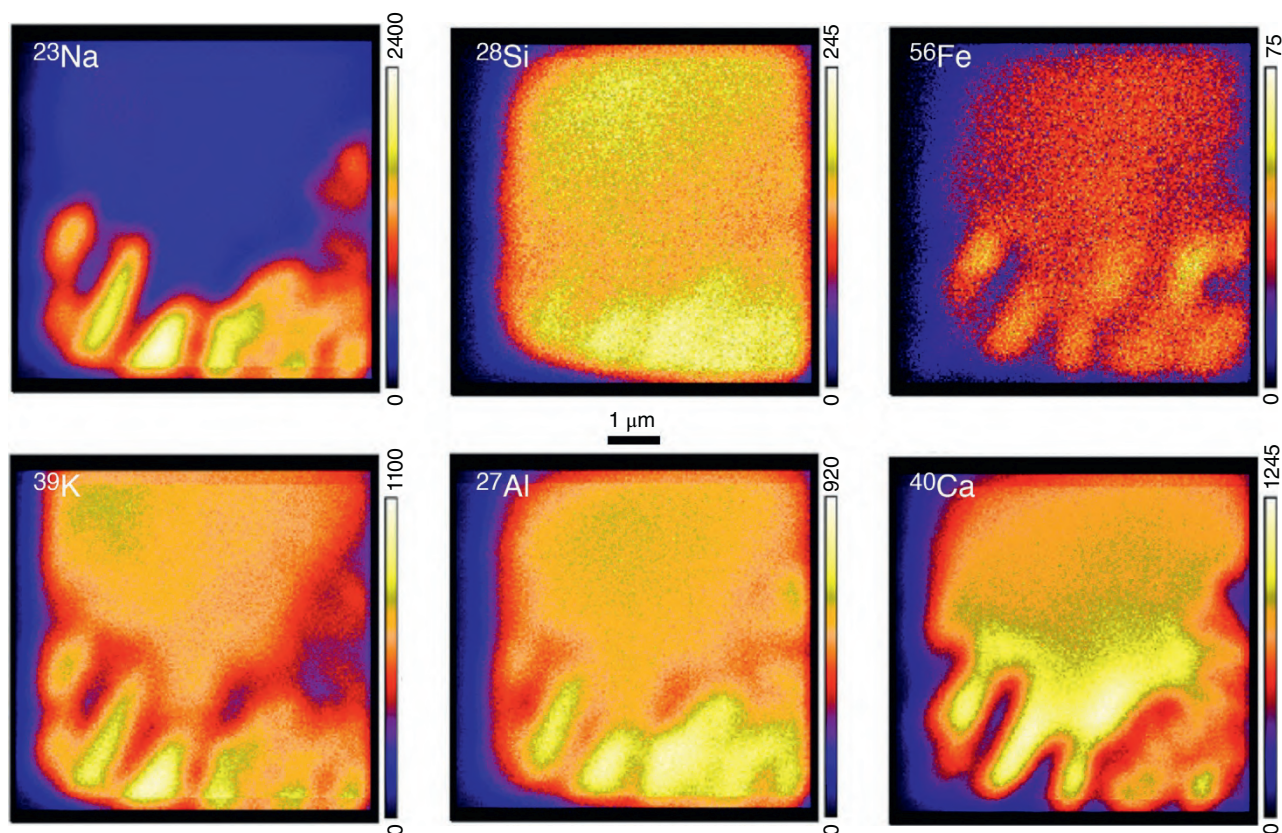


Figure 2 Dendrites of a nepheline of composition $(\text{Na}_{0.7}\text{K}_{0.2}\text{Ca}_{0.07}\text{Fe}_{0.05})\text{Al}_{0.92}\text{Si}_{1.05}\text{O}_4$ visualized by enrichments in Na, K, Al, and Si in nanoSIMS analyses of an aluminosilicate glass partially crystallized at 850 °C. Residual glass enriched in Ca and Fe around the dendrites, from which wollastonite $[(\text{Ca}, \text{Fe})\text{SiO}_3]$ crystallizes upon further annealing. Source: Cochard [15].

$[\text{C}_{21}\text{H}_{16}\text{Br}_2\text{O}_5\text{S}]$. Addition of CaCO_3 then causes interfering ions to precipitate and allow them to be removed by filtration. The filtrate itself is titrated with a NaOH solution against a defined pH value. The B_2O_3 concentration can be determined in this way for glasses with B_2O_3 contents higher than 0.5 wt %.

Ultraviolet–visible (UV–Vis) spectroscopy is another method, which relies on the property of certain ions (e.g. Fe^{3+} , Mn^{3+}) to form colored complexes with organic reagents such as 2,2′-bipyridine $[\text{C}_{10}\text{H}_8\text{N}_2]$. According to Beer–Lambert law, the intensity of light absorption at the appropriate wavelengths then is proportional to the concentration of these ions. With suitable standards, a calibration curve can thus be set up in order to determine the concentration of unknown samples [17].

These colored complexes are prepared in two ways. For 0.01–2.5 wt % B_2O_3 contents, azomethine-H $[\text{C}_{17}\text{H}_{12}\text{NO}_8\text{S}_2]$ is used to form a yellow boron complex in the aqueous solution formed upon dissolution of the NaOH-melted sample. In the 0.01–1 wt % range, the complexing agent can be curcumin $[\text{C}_{21}\text{H}_{20}\text{O}_6]$, a red-colored complex. The sample is

first melted with Na_2CO_3 or with a 1 to 4–6 ratio with a low-melting Na_2CO_3 – K_2CO_3 mix and possibly also with flux such as NaNO_3 . After cooling the solid obtained is dissolved in HCl, some H_2SO_4 is added, and the solution is heated and dehydrated. Formation of rosocyanine (in dissolved state), $[\text{B}(\text{C}_{21}\text{H}_{19}\text{O}_6)_2]\text{Cl}$, is achieved upon addition of curcumin. Finally boron is determined with UV–Vis spectroscopy after dissolution of the product in a water–ethanol mixture.

The third common method for boron analyses is ICP–MS. Although HF digestion leads to formation of volatile BF_3 , which causes the analysis to be too low, trace amounts of boron can be captured in the solution with complexing agents. Boron concentrations lower than 0.1 wt % can be determined in this way. For higher contents, the sample must be digested in NaOH–KOH solutions, but the method has two limitations: like for all ICP–MS analyses, the solution must be highly diluted, which causes uncertainties in the actual dilution factor, and, in addition, boron may be the source of a memory effect by first diffusing into and at a later stage out of ICP tubes and container walls.

7.2 Lithium

Glasses containing trace amounts of lithium can be digested in HF. If their Li concentrations are high, a sodium peroxide [Na_2O_2] digestion is recommended. The highly saline solution must then be diluted before quantification by ICP-OES or F-AAS.

7.3 Fluorine

At concentrations higher than 0.1 wt %, fluorine can be quantified with WDXRF either directly, if the sample is flat, or ground and pressed as a pellet otherwise. At lower contents, ion chromatography can be used after soda and potash digestion of the sample at 800 °C and dilution of the quenched product in water. The fluorine anion takes a specific time to pass through the chromatography column so that the F concentration can be determined at the end of the column by a thermal conductivity detector. The quantification limit is 0.1 µg/l equivalent to 10 mg/kg in glass.

Another method relies on an ion-selective electrode, which consists of an active material, typically LaF_3 for F analyses, placed in contact with the same solution as prepared for ion-chromatography analysis. At the phase boundary an electromotive force (emf) builds up, which in principle follows Nernst equation and is proportional to the logarithm of the activity of F ions. As a difficulty, at elevated F levels, large changes of concentration correspond to small changes in emf only. In addition, ions such as Ca^{2+} , Al^{3+} , or Fe^{3+} form hardly soluble fluorides that escape analysis. To avoid this trouble, elements can be masked with buffer solutions so that they will not precipitate.

As a matter of fact, pyrohydrolysis is one of the methods with which interfering ions can be separated in F-content determinations. When the finely ground sample is heated in a tube furnace in an atmosphere of superheated water vapor, the volatile fluorides are released and fed into an absorption solution. Alternatively, sinter extraction can be used. The glass sample is melted in a Na_2CO_3 –ZnO mixture at 1000 °C. After cooling, the sample is dissolved in water and filtered, and the remaining carbonates are decomposed in HCl. The fluoride limit of quantification is 10 mg/kg.

7.4 Ferrous Iron

Iron redox ratios are of crucial importance in the production of white glass and also play a fundamental role in petrology. In academic research, extensive use is made of Mössbauer and XANES spectroscopies (Chapter 2.2) because these provide in addition detailed structural information on the local environment of Fe^{2+} and Fe^{3+}

ions, but these methods are of course inappropriate for routine chemical analyses. A standard procedure consists of determining the total iron content, for instance, by XRF or ICP-OES analysis, and then deriving Fe^{3+} contents from the measured Fe^{2+} .

The three methods commonly used for this purpose all involve UV-Vis spectrometry [18].

The simplest makes use of a glass plate with parallel faces of known thickness for which extinction at 1054 nm is determined. According to Lambert–Beer law, the extinction is a function of the extinction coefficient of Fe^{2+} , the length of the optical path, and Fe^{2+} concentration. For a given glass composition, the extinction coefficient must of course be determined independently.

In a second method, the specimen is digested in a mixture of HF and H_2SO_4 , and Fe^{2+} ions are then converted into a pink complex by addition of phenanthroline [$\text{C}_{12}\text{H}_8\text{N}_2$] whose extinction is determined at 510 nm. Preferably the whole procedure is carried out under an inert atmosphere to prevent oxidation of Fe^{2+} in air. Alternatively, however, the sample may be digested in air, provided the solution is stabilized with nitrilotriacetic acid [$\text{C}_6\text{H}_9\text{NO}_6$] and measured directly in polystyrene cuvettes cooled with ice.

8 Resistance to Chemical Attack

In spite of its celebrated chemical inertness, glass is actually attacked by a variety of liquids. In industry, it is of particular importance to categorize glass into different classes with respect to hydrolytic, acid, and alkali resistance.

8.1 Hydrolytic Resistance

Special glasses have been designed for the pharmaceutical and medical sectors where patients must be protected from container impurities that might end up in drugs (Chapter 7.7). The resistance against water of the glass of interest is thus tested with standardized procedures to determine to which of the five classes that have been defined it belongs. The test determines the rate of Na^+ ions released from the color change of an indicator when the resulting alkaline solution is neutralized with HCl.

For the interior surfaces of glass containers, a given volume of the specimen is filled with water of defined purity, covered with an aluminum foil, and subjected to a temperature program reaching a maximum temperature of 121 ± 1 °C for 60 minutes [19]. The dissolution of mainly alkali, alkaline earth, and silicon ions results in a pH increase. The resistance class is then determined from the amount of HCl used to titrate the solution against methyl red until a color change is observed.

The hydrolytic stability of soda-lime glass can be improved by a surface finish applied during production. To check whether a glass has been surface-treated, a previously examined specimen is filled with a 1 : 9 mixture of HF and HCl and filled again with water after subsequent cleaning. The glass is then classified as surface-treated if the new titrimetric values are five to ten times higher than the first ones.

In another test the effect of temperature on hydrolytic resistance is determined on 100 g of glass carefully crushed with a hammer and steel mortar. The powder is passed through a magnetic separator to remove traces of metals from the mortar. The test is then made on the 300–500 µm sieved fraction cleaned in acetone, weighed in a vessel of defined volume, and heated at 98 °C for 60 minutes and titration as described above. For resistance tests at higher temperatures, the procedure must be modified in that the selected 300–425 µm sieved fraction is autoclaved for 30 minutes at 121 ± 1 °C [20] under strictly controlled conditions.

Alternatively, alkali and alkaline earth elements can be determined spectroscopically and then converted to Na₂O equivalents. The results obtained for a F-bearing glass by different methods are compared in Table 3. The cation (Na, K, Ca) contents determined by ICP-OES have been converted into Na₂O equivalents and summed up to yield a value 74.8 µg/g that deviates considerably from that determined by titration (53 µg/g). The discrepancy is caused by fluorine ions, which act like an acid (HF) in an aqueous solution neutralizing hydroxyl ions formed in the presence of alkali and alkaline earth ions. When the measured fluoride is converted into

Na₂O equivalents (26 µg/g) and added to the titrated Na₂O equivalent of hydrochloric acid (53 µg/g), both results are similar. The example demonstrates that determination of the hydrolytic class by titration is problematic for F-bearing glasses although it is allowed by the standardized procedure.

For pharmaceutical glass the aqueous solution obtained during the investigation of the hydrolytic class has to be analyzed with regard to As content. According to currently valid pharmaceutical regulations, quantification has to be carried out via hydride generation atomic absorption spectroscopy (HG-AAS), although ICP-OES is similarly suitable for this purpose. In HG-AAS a quartz cuvette is put on the burner of the F-AAS. The sample is reduced in a liquid–gas separator by a reducing agent (NaBH₄). Thanks to the separation of the gas from the liquid matrix, a very low limit of quantification is achieved. The measurement is carried out in a sequential mode, which results in extended measurement times at high consumption of chemicals and sample material. With this technique, other elements such as Sb and Hg can be analyzed in glass after digestion.

8.2 Acid and Alkali Resistance

Acid resistance strongly depends on surface properties. For determining it, the test specimen is cleaned with water and 2-propanol, dried, weighed, placed into a PTFE net, and immersed into boiling HCl ($c_{\text{HCl}} = 6$ mol/l) without being in contact with the walls of the vessel. After six hours, it is removed, rinsed, dried, optically inspected with regard to visible changes, and finally weighed and classified into one of four acid resistance classes from the measured mass loss. A similar procedure is followed for alkali resistance with a three hour immersion in a caustic solution:

1 : 1 mixture of Na₂CO₃ ($c_{\text{Na}_2\text{CO}_3} = 0.5$ mol/l) and a NaOH ($c_{\text{NaOH}} = 1$ mol/l) solution at 110 °C [21].

8.3 Leaching of Pb and Cd

For glass hollowware in contact with food, the rates of release of lead and cadmium must be checked. For this purpose, the hollow glassware is filled with a 4% (V/V) acetic acid solution for 24 hours at 22 °C [22]. The rate of leaching is then determined from the concentrations of lead and cadmium as measured by ICP-OES, F-AAS, or any other equivalent method. Producers of lead crystal glass are meeting the required thresholds for Pb and Cd. Nevertheless demand for lead crystal glass is strongly decreasing, resulting in a limited number of producers.

Table 3 Comparison between hydrolytic-resistance tests made for a F-bearing glass as determined by ICP-OES, titration, and ion chromatography.

Element	ICP-OES	
	Concentration (µg/g)	Na ₂ O Equivalent(µg/g)
Na	32	43.1
K	4.9	3.9
Ca	18	27.8
Sum		74.8
Titration		
	V(HCl) (ml)	
	0.17	53
Ion chromatography		
F	16 (µg/g)	26

9 Analyses of Glass Defects

Reams or inclusions are among the most common glass defects. They account for high economic damage, so understanding their formation is very important to the glassmaker. They are caused either by impure raw materials, containing, for example, refractory heavy minerals, or by the glass-melting furnace or other parts of the plant (Chapter 1.2). They must appear at the glass surface to be investigated. In addition to SIMS described above, the following methods can be used.

9.1 Micro-X-Ray Fluorescence

In micro-X-ray fluorescence (μ -XRF), the X-ray beam is focused to a small diameter of typically 50–200 μm . One can thus analyze tiny spots on a sample identified by means of a camera either individually (“spotting”) or by applying a grid of individual measurement spots on a pre-defined area of the sample (“mapping”). This technique is typically applied in glass defect analysis. Inclusions of foreign particles (Al_2O_3 , ZrO_2) in the glass can deliver important information on the state of a glass-melting furnace or on contamination of raw materials, for instance, by heavy minerals (chromite, barite, etc.).

9.2 Laser-Induced Breakdown Spectroscopy

The other method is LIBS with which a highly energetic laser pulse vaporizes and atomizes the sample surface at a very small scale. The radiation emitted by the plasma formed is then analyzed with a spectrometer [23]. Important advantages of the method are that it requires very little or no sample preparation and that only a tiny amount of the sample material is removed in a layer-by-layer fashion. In addition, it is a very fast method that allows for a depth-resolved profiling of the chemical composition. Owing to instrument design, however, the spectrometer and laser are not in the same optical axis, which means that the intensity of the emitted radiation reaching the detector decreases when the penetration depth increases. Besides, the reproducibility of LIBS is often limited by variations in the laser spark and resultant plasma. One should take into account that LIBS is not suitable for bulk analysis of not perfectly homogeneous materials since only a very limited volume is probed.

9.3 Scanning Electron Microscopy with Energy-Dispersive X-Ray Analysis

For analyses of glass defects, a very precise quantification is in fact not required. If SEM-EDS has, for instance, a good spatial resolution of less than 1 μm , the sample

has to be sputtered, which is time consuming. In contrast, LIBS and μ -XRF have a lower spatial resolution of 50–200 μm , so they are suited best for determining heavier elements or bigger defaults.

For example, analyses of the glass defect shown in Figure 3 and made with SEM-EDS indicate a significant increase of the Al_2O_3 and ZrO_2 concentrations (Table 4). Since Al and Zr oxides are typical refractory materials used in the construction of glass-melting furnaces, one must conclude that the defect likely originated from the plant and not from the raw materials used.

10 Perspectives

EDXRF and AAS will likely take a leading role in analyses of industrial glasses. The former allows for quick analyses thanks to simultaneous element detection by solid-state semiconductor detectors, which is cost efficient with a compact design and a lower power X-ray tubes that are

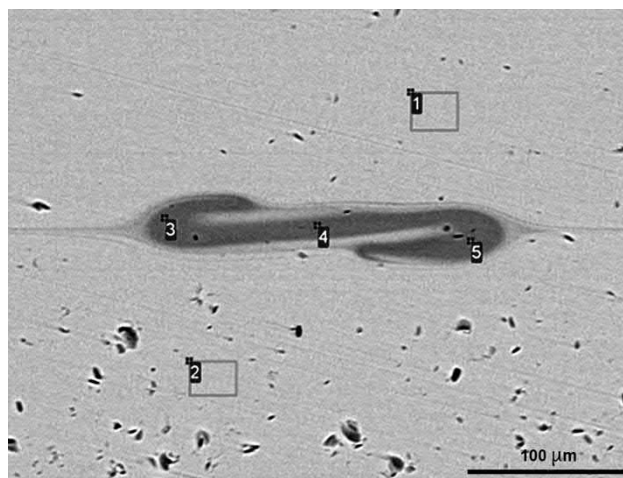


Figure 3 Glass defect: streak in a float glass as seen and analyzed (Table 4) by SEM-EDS.

Table 4 Defect in a float glass as revealed by anomalous chemical analyses made by SEM-EDS.

Point	Na ₂ O	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	ZrO ₂	BaO
1	10.71	1.12	72.99	3.37	5.77	0.00	6.04
2	10.64	1.27	72.64	3.39	5.82	0.00	6.23
3	9.82	10.32	68.13	4.99	2.39	0.68	3.68
4	9.86	12.39	66.76	5.28	1.84	0.69	3.18
5	10.40	15.69	63.04	5.66	1.32	0.88	3.01

Points 3, 4, and 5 within the glass defect.

less expensive than wavelength-dispersive instruments, which do yield a higher resolution. Taking into consideration the rapid advances made in detector technology (e.g. silicon-drift detectors requiring only Peltier instead of liquid-nitrogen cooling), one can even expect that their resolution will keep improving in the next generation of instruments.

On the other hand, almost all elements can be analyzed without interferences and with good sensitivity with AAS whose main drawback has been the sequential and, therefore, time-consuming mode of measurement caused by frequent lamp changes. The introduction of continuously emitting xenon short-arc lamps as light sources has helped to overcome this limitation at the same time that the use of CCD instead of photomultiplier detectors has greatly improved the efficiency of the instruments. As to the lower sensitivity of CCD detectors, it is more than compensated by the high radiation intensity of xenon short-arc lamps. These two innovations allow for simultaneous detection of absorption spectra, which in turn result in improved linearity and signal-to-noise ratio, in lower limits of quantification, and, of course, in timesaving benefits. In other words, AAS could regain in this way the situation it has lost lately at the expense of ICP-OES in systematic analysis of major elements, in which case it would no longer be restricted to determinations of trace concentrations of coloring (Ni, Cr, Mn, Co, Cu, V, Fe, Mo) or environmentally and food-relevant (Pb, Cd, Ba, As, Sb, etc.) elements. Whether or not this novel technique actually finds widespread use in glass analytics will thus be seen in a near future.

Finally, another striking feature of the evolution of chemical-analysis methods consists in the tremendous increase in spatial resolution: Accurate results can now be obtained for samples smaller than 1000 nm^3 , which are thus about 10^{18} times smaller than the specimens originally required by gravimetric methods (in analyses that are in addition performed about 1000 times faster). To take full advantage of such resolutions, however, it should not be overlooked that some specific preparation methods should in parallel be used for preparing the samples investigated in a way commensurate with the actual analytical resolution, as illustrated in Chapter 5.12 for corrosion reactions.

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5.2

Phase Equilibria and Phase Diagrams in Oxide Systems

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1 Introduction

In glassmaking, phase changes are of fundamental importance since the process most commonly involves the melting of a mixture of solid starting materials (Chapter 1.1). Phase heterogeneities in glass (e.g. crystal inclusions, gas bubbles, etc.) are usually regarded as defects (Chapter 1.2), so glass-forming melts are usually kept at temperatures much higher than that thermodynamically needed to ensure complete melting. Special measures are then taken to avoid crystallization of the melt and/or its unmixing to immiscible liquid phases upon cooling. In contrast, the production of special types of glasses (e.g. turbid, opaque, opalescent) and of glass ceramics requires controlled formation of solid–liquid or liquid–liquid heterogeneous phase assemblages. In any case, whether nucleation of new phases (phase separation) should be avoided or controlled, an in-depth knowledge of crystal–liquid and liquid–liquid phase equilibria in specific glass-forming systems is crucial. Hence, phase diagrams displaying melting/crystallization relationships in temperature–composition (T – x) coordinates play the same fundamental role in scientific studies and production of glass as topographic maps in geography and navigation.

Although until the 1960s phase diagrams could be determined only experimentally, they did strongly rely on fundamental concepts of chemical thermodynamics as pioneered by J.W. Gibbs (1839–1903) and, in particular, on the phase rule. It is thus appropriate to begin this chapter with a brief review of the theoretical concepts on which phase diagrams are based. The different types

of diagrams resulting from varying mutual solubility between components in the solid and liquid phases are then described. Special attention is given to liquid immiscibility and liquid–solid phase separation in glass-forming systems, but liquid–gas equilibria will not be described in view of the very low solubility of volatiles in glass-forming melts at room pressure (Chapter 5.5). Finally, some examples of particular importance for glass-making are discussed in greater detail.

In preamble, however, we first note that the sluggishness of chemical reactions in viscous glass-forming systems generally prevents phase transitions from being observed by abrupt changes in physical properties. Ever since the beginning of the twentieth century, the quenching method has thus been used: a sample of a given composition is heated at an appropriate series of precisely measured temperatures, quenched, and observed under the microscope for detection of the very first occurrence of glass (at the *solidus* temperature) and the total disappearance of crystals (at the *liquidus* temperature). It goes without saying that the procedure is very tedious if experimental brackets of a few degrees are to be obtained. In industry, this is why it is common practice to run instead simultaneously a number of samples of the same composition in a gradient furnace (Chapter 5.1).

Additional experimental difficulties arise from the significant volatility of some elements (e.g. the alkalis), the high melting temperatures of some components (e.g. the alkaline earth oxides), or redox changes of transition elements such as iron (Chapter 5.6), which imply to control not only temperature but also the oxygen fugacity. Nevertheless, phase equilibria have been established with great care and accuracy sufficient for most practical and theoretical applications. Even complexities such as liquid unmixing was discovered as early as the 1920s in alkaline earth silicates in spite of the temperatures higher than 1600 °C at which it takes place [1]. In brief, phase

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diagrams are indispensable reference tools, so special compilations have long been available to glassmakers and ceramists, first as books [2] and now through electronic databases [3].

2 Thermodynamic Principles

2.1 Gibbs Free Energy

The macroscopic state of a glass-forming system can, in principle, be defined with little or no reference to microscopic states at the atomic and molecular level, but some discussion of molecular species and chemical bonds is practically unavoidable when thermodynamic methods are applied to systems with chemical reactions (Chapter 5.3). First and foremost, however, the importance of thermodynamic laws and their great usefulness in chemistry and materials science lie in their theoretical ability to predict the direction of chemical reactions and the stable state of a system of a given chemical composition at given pressure and temperature. With thermodynamic methods, one can predict the stable macroscopic state of the system, e.g. the nature and chemical compositions of stable solid, liquid, and gaseous phases, without needing to consider the previous macroscopic states and the processes that led to the final state of interest.

Laboratory experiments and technological processes are generally performed at constant temperature and pressure, e.g. one atmosphere. If the temperature is changed during the process, sensible measurements are usually done after the change is over, when the temperature has become uniform in all parts of the system. Systems without internal pressure and temperature gradients are called isobaric–isothermal. Stable macroscopic states and the direction of possible chemical reactions in such systems are predicted by the analysis of a thermodynamic potential, the *Gibbs free energy* (G), which is defined as

$$G = H - TS. \quad (1)$$

In Eq. (1) H is the enthalpy, which, under isobaric conditions, is equivalent to the loss or gain of heat (thermal energy) to or from the surroundings of the system; T is the absolute temperature; and S is the entropy of the system. Although G is measured in units of energy, the traditional name is somewhat misleading because the energy conservation law does not apply to G , so G differs from the internal energy U in that important respect. Alternatively, *Gibbs function* has been recommended to avoid the confusion, but the traditional term remains in broad use.

Because H , T , and S are all state functions, so is G . It quantitatively defines the equilibrium state of the system. As, for instance, caused by a pressure or a temperature

variation, a change in the state of a system results in a change of its Gibbs free energy ΔG , which in turn combines enthalpy and entropy changes, ΔH and ΔS :

$$\Delta G = \Delta H - T\Delta S. \quad (2)$$

Notably, in an isobaric system,

$$\Delta H = -Q = -T\Delta S_{\text{ext}}, \quad (3)$$

where Q is the heat transported from outside the system (hence the negative sign) and ΔS_{ext} is the external entropy change in the system surroundings. From Eqs. (2) and (3), it follows that

$$\Delta G = -T\Delta S_{\text{ext}} - T\Delta S = -T\Delta S_{\text{tot}}, \quad (4)$$

where ΔS_{tot} is the overall change of entropy within and outside the system. According to the second law of thermodynamics, any spontaneous, self-sustaining process must result in an increase of S_{tot} or, in other words, must have a positive ΔS_{tot} . Therefore, from Eq. (4), it follows that ΔG must be negative for spontaneous changes of state:

$$\Delta G = \Delta H - T\Delta S < 0, \quad (5)$$

so the stable macroscopic equilibrium state is the one with the lowest G at given pressure, temperature, and chemical composition.

Like H and S , the Gibbs free energy is an extensive (additive) variable. For a generalized reaction



its variation ΔG_r is defined as a sum of the Gibbs free energy of the products minus that of the reactants:

$$\Delta G_r = G_C + G_D - G_A - G_B. \quad (7)$$

The reaction spontaneously proceeds to the right toward the products if

$$G_C + G_D < G_A + G_B, \quad (8)$$

and in the opposite direction toward the reactants in case

$$G_C + G_D > G_A + G_B. \quad (9)$$

The reactants and products can be individual phases or components taking part in homogeneous reaction. At equilibrium, ΔG_r should be 0:

$$\Delta G = \Delta H - T\Delta S = 0. \quad (10)$$

Processes relevant to glassmaking mostly take place at high temperatures where the contribution of the product $T\Delta S$ is often significant and the sign and value of ΔG thus strongly depend on those of ΔS . For example, melting of a crystalline solid to an isochemical liquid is characterized by a significant and positive entropy change, ΔS_m . When crystals and melt are at equilibrium, $\Delta G = 0$ and a positive ΔS_m implies that melting is strongly endothermic (ΔH_m positive and large). It also follows that melting will be spontaneous at $T \geq \Delta H_m / \Delta S_m$.

2.2 Phase Rule

In multicomponent systems, the Gibbs free energy is expressed as a sum of partial molar energies (chemical potentials) of individual components, μ_a , multiplied by the number of moles of each component N_a present in the system. Thus, for a system with n components,

$$G = \sum_a^n \mu_a N_a. \quad (11)$$

The conditions for equilibrium in heterogeneous (multiphase) system require that all intensive variables (e.g. pressure, temperature, and chemical potentials of all the components) should be equal in all phases. Thus, in a system with n components and p phases,

$$T^1 = T^2 = T^3 = \dots = T^p, \quad (12a)$$

$$P^1 = P^2 = P^3 = \dots = P^p, \quad (12b)$$

$$\mu_a^1 = \mu_a^2 = \mu_a^3 = \dots = \mu_a^p, \quad (12c)$$

$$\mu_b^1 = \mu_b^2 = \mu_b^3 = \dots = \mu_b^p, \quad (12d)$$

...

$$\mu_n^1 = \mu_n^2 = \mu_n^3 = \dots = \mu_n^p. \quad (12e)$$

The set of equations implies a fundamental relationship between the number of independent intensive variables (degrees of freedom f), the number of components n , and the number of phases p in a heterogeneous multicomponent system:

$$f = n - p + 2. \quad (13)$$

This relationship is the *phase rule*. Its fundamental implication is that the maximum number of phases in a closed system at equilibrium cannot exceed $n + 2$ because negative values for f would be by definition meaningless. A physically viable system must contain at least one component. With pressure and temperature as the two independent variables in Eq. (13), the maximal number of phases in a single-component system thus is 3. The maximal assemblage of $n + 2$ phases represents an invariant ($f = 0$) phase equilibrium, which occurs at a unique combination of values of all intensive variables. None of the values can be changed without disappearance of at least one phase.

Although they have a considerable importance in earth sciences, the effects of pressure on crystal–liquid and liquid–liquid phase transitions and equilibria will not be considered in this chapter because technological processes, glassmaking included, are generally carried out at one atmosphere. If pressure is excluded from the list of intensive variables, the equation for the phase rule then takes the form

$$f = n - p + 1, \quad (14)$$

which will be used in the following discussions of phase equilibria diagrams.

2.3 Gibbs Free Energy of Mixing

From a thermodynamic point of view, a homogeneous solution is stable when its Gibbs free energy is lower than that of mechanical mixture of its components. The energy difference between the solution and the equivalent mechanical mixture is the Gibbs free energy of mixing ΔG_m . Mixing relationships between nonideal components, i.e. chemically interacting with one another, are often discussed in terms of the simple regular solution model, which assumes that the components mix completely at random even though they interact with a positive or negative enthalpy of mixing depending on whether the overall interactions are repulsive or attractive. Although the model is a crude approximation to real solutions relevant for glass-forming systems, it will illustrate nicely some fundamental principles of mixing and unmixing between components A and B.

Conventionally, the chemical composition of the system is expressed in terms of the mole fractions of the components x_A and x_B :

$$x_A = \frac{N_A}{N_A + N_B}, \quad (15a)$$

$$x_B = \frac{N_B}{N_A + N_B}, \quad (15b)$$

$$x_A + x_B = 1, \quad (15c)$$

where N_A and N_B are the numbers of moles of A and B in a given composition. Like any other type of Gibbs free energy of mixing, ΔG_m is made up of enthalpy (ΔH_m) and entropy (ΔS_m) terms:

$$\Delta G_m = \Delta H_m - T \Delta S_m. \quad (16a)$$

For an *ideal* solution, the former is zero and the latter is given by

$$\Delta S_m = -R(x_a \ln x_a + x_b \ln x_b), \quad (16b)$$

where R is the gas constant. Because mole fractions are lower than 1, the logarithm term is negative, and, therefore, ΔS_m is positive. As for the enthalpy of mixing, it is given by

$$\Delta H_m = \alpha x_a x_b, \quad (17a)$$

where

$$\alpha = NZE_{ab}, \quad (17b)$$

and E_{ab} is an interaction energy between components A and B, Z is the coordination number of the interacting

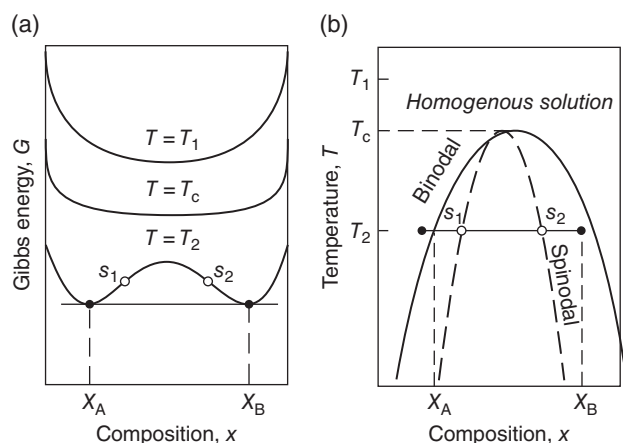


Figure 1 Binodal and spinodal in a binary system A–B. (a) Gibbs free energy (G) versus composition (x) curves for the consolute temperature T_c and two other temperatures either higher (T_1) or lower (T_2) than T_c . The spinodal is defined by the inflexion points s_1 and s_2 , the compositions of the immiscible phases A_s and B_s by those at which a line is twice tangent to the G curve. (b) Two-phase region $A_s + B_s$, binodal and spinodal in T – x coordinates.

components, and N is Avogadro's number. If α is negative, so are ΔH_m and ΔG_m , and the solution is stable at any temperature and composition. If the interaction parameter is positive, the balance between enthalpy and entropy terms (which oppose and favor mixing, respectively) changes with temperature. In Figure 1a, ΔG_m curves are plotted versus composition x at three different temperatures $T_1 > T_c > T_2$. At T_1 the G – x curve is concave, whereas at T_2 there are two minima and a local maximum in the middle. Between the minima, the original solution unmixes into two coexisting subsolutions A_s and B_s because the Gibbs free energy of the homogeneous phase is greater in that composition interval than that of a mechanical mixture of A_s and B_s . The positions of the minima along the x axis change with temperature, the compositions of A_s and B_s moving further apart with falling temperatures. In T – x coordinates, the loci of minima plot along a convex curve, the *binodal* (Figure 1b). The temperature T_c represents the maximum point of the binodal curve when two solutions merge into one, so both temperature and point are termed *critical* or *consolute*. In the context of the regular solution model,

$$T_c = \frac{\alpha}{2R}. \quad (18)$$

Therefore, measurements of T_c provide a means for evaluating the interaction parameter α .

The inflexion points s_1 and s_2 in the G – x curves (Figure 1a) are defined by the second derivative $(\delta^2 G / \delta x^2)_{T,P} = 0$. Their loci define in the T – x plot a convex curve, the *spinodal* (Figure 1b), which delineates two different mechanisms of unmixing (Chapter 5.4). In

compositional intervals between the binodal and spinodal, unmixing proceeds via nucleation and growth and is hampered by thermodynamic barriers associated with nucleation. The nuclei of a new phase are viewed as small aggregates of atoms formed by random compositional fluctuations δx . Compositional fluctuations smaller than a certain critical value produce increases of Gibbs free energy and are, therefore, thermodynamically unstable. In contrast, there is no thermodynamic barrier for phase separation within the spinodal region as the Gibbs free energy change is negative for an infinitesimal fluctuation. Kinetic limitations are the same for both mechanism of unmixing, however, because they arise from material transport and dynamic parameters such as diffusion rates and viscosity.

3 Basic Topological Types of Binary T – x Diagrams

3.1 General Remarks

Binary (two-component) mixtures including liquid (melt) among the phases are the simplest cases of systems relevant to glassmaking. As a matter of fact, they have a more general interest because atomic interactions have a mainly pairwise nature in oxide solutions (Chapter 2.8). In other words, one can consider that higher-order effects have only a small influence in ternary or multicomponent systems and that, at least qualitatively, information drawn from binary mixtures can throw valuable light on phase equilibria in more complicated systems.

The Gibbs free energy and the binodal and spinodal curves defined by the regular solution model are symmetrical along the x axis. These features are rarely observed in silicate and other glass-forming systems, however, where binodal curves are usually strongly asymmetric and imply more complex interactions between the components. In this respect, an important point is that both strongly positive and negative interactions result in phase separation. The difference is that the former causes unmixing whereas the latter yields formation of intermediate compounds. This contrast is typically observed in binary silica–metal oxide systems where liquid immiscibility is found on the SiO_2 -rich parts and compound formation beginning at SiO_2 contents ranging from 20 to 50 mol %. This observation does not contradict the aforementioned binary nature of atomic interactions. It indicates instead that interactions of silicon with other cations depend on its Q^n speciation (Chapters 2.1 and 2.4), being repulsive for $n = 4$ species and attractive for the lowest values of n .

Another fundamental feature is the existence or lack of long-range order in a phase. As a rule, element mismatch is of course much more easily accounted for in liquids

than in crystals, so mutual solubility is systematically higher in the former than in the latter. Consequently, complete miscibility in solid solutions is excluded in systems with limited melt miscibility. Likewise, intermediate compounds are not to be found in compositional regions of liquid immiscibility.

Depending on the mutual solubility of components in the liquid and solid phases and the existence or lack of reactions between the solids, the T – x phase diagrams of the binary systems fall into several basic topological types. Those types of diagrams and phase equilibria, which they illustrate, will now be discussed in the context of Gibbs free energy variations with temperature T and composition x expressed in molar units or, alternatively, in mass units for convenience in practical applications. In conventional binary T – x diagrams, temperature is plotted along the vertical axis at the right angle to the composition line. Compositions along the latter are plotted in bar-centric coordinates.

3.2 Complete Miscibility in Melt and No Solubility or Reaction Between Solids

Consider a generalized system of components A and B, which are completely miscible in the melt L and form the immiscible crystal phases A and B. At constant pressure, its Gibbs free energy is a function of temperature and composition, $G = f(T, x_A, x_B)$. In a G – x diagram (Figure 2), the Gibbs free energy G^s of the solid phase assemblage A + B varies with composition along the straight line connecting those of the crystalline phases G^A and G^B . The linear G – x relationship is characteristic for mechanical mixture of phases, which do not mix or react. The equation of the line is

$$G^s = x_A G^A + x_B G^B, \quad (19a)$$

or, because $x_A + x_B = 1$,

$$G^s = (G^A - G^B) x_A + G^B. \quad (19b)$$

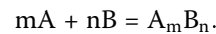
A plot of Gibbs free energy of the melt G^L versus composition is a concave curve (Figure 2). The G – x diagram in Figure 2a thus represents the situation where the liquid is stable but the solid phases are not. This situation exists at temperatures above the melting points of crystal phases A and B. With decreasing temperature, the Gibbs energies of the solid phases and melt increase, but G^L increases faster than G^A and G^B because the entropy of the melt is greater. At some temperature T_2 (Figure 2b), the Gibbs energies of the solid and liquid phases for the pure component B become equal, so the solid B begins to crystallize. As temperature decreases, the melt in equilibrium with solid B becomes gradually depleted in this component. In a G – x diagram, the

equilibrium composition of the melt (L_1) is defined by the intersection of a tangent line drawn from the point G^B with the curve G^L (Figure 2c).

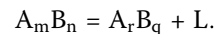
Below the melting point T^A of A, crystallization of this phase becomes possible on the left side of the diagram where the concentrations of this component in the melt are high and melts equilibrated with solids A and B are defined in the same way by tangent lines (Figure 2d). The loci of melt compositions in equilibrium with the solids A and B are represented in T – x space by two liquidus curves (Figure 2g). In a binary isobaric system, two-phase equilibria L + A and L + B are univariant. The curves intersect at a point of the invariant equilibrium L + A + B, the eutectic (point E in Figure 2e and g). Below the eutectic temperature T_E , the liquid phase is unstable because the Gibbs free energy of the solid assemblage A + B is lower than G^L at any bulk composition x (Figure 2f). The horizontal line going through the eutectic point E in Figure 2g is the solidus line. Below it, the system has totally crystallized.

3.3 Complete Miscibility in Melt and Binary Solid Solution

A binary system may include one or several intermediate compounds resulting from chemical association between the solids:



If an intermediate compound has a fixed composition or, in other words, is immiscible with other solid phases, it must melt at a fixed melting point either isochemically (congruently) to the liquid of the same composition or incongruently to a liquid of a different composition and another solid phase:



Phase diagrams with congruently and incongruently melting binary compounds are presented in Figure 3a and b. Congruently melting compounds, such as A_mB_n in Figure 3a, divide the diagram into two parts, which can be considered as independent eutectic-type subsystems ($\text{A} - \text{A}_m\text{B}_n$ and $\text{A}_m\text{B}_n - \text{B}$ in Figure 3a). Notably, eutectic points in adjacent subsystems (E_1 and E_2 in Figure 3a) are not at the same temperature because the stable coexistence of more than two solid phases with a liquid in an isobaric binary system does not comply with the phase rule.

In Figure 3b, the intermediate compound A_mB_n melts incongruently into the solid phase A and liquid L of composition P, which, in agreement with mass-balance considerations, is richer in component B than the solid A_mB_n . The invariant phase equilibrium $\text{A}_m\text{B}_n + \text{A} + \text{L}$ corresponds to the peritectic point P.

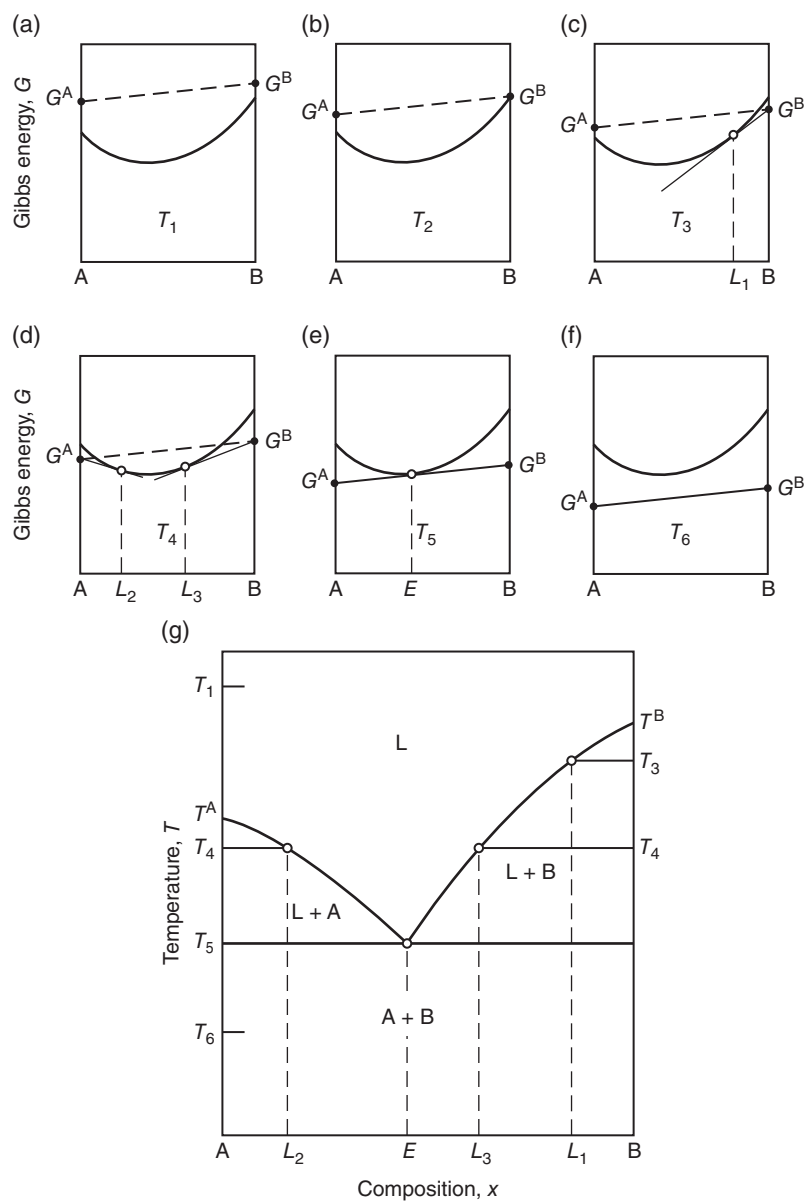


Figure 2 Binary system A-B with end members miscible only in the melt. (a–f) Gibbs free energies of the solid and liquid phases as a function of composition for temperatures decreasing from T_1 to T_6 . (g) Derived eutectic-type phase diagram (L = liquid, T_E = eutectic temperature).

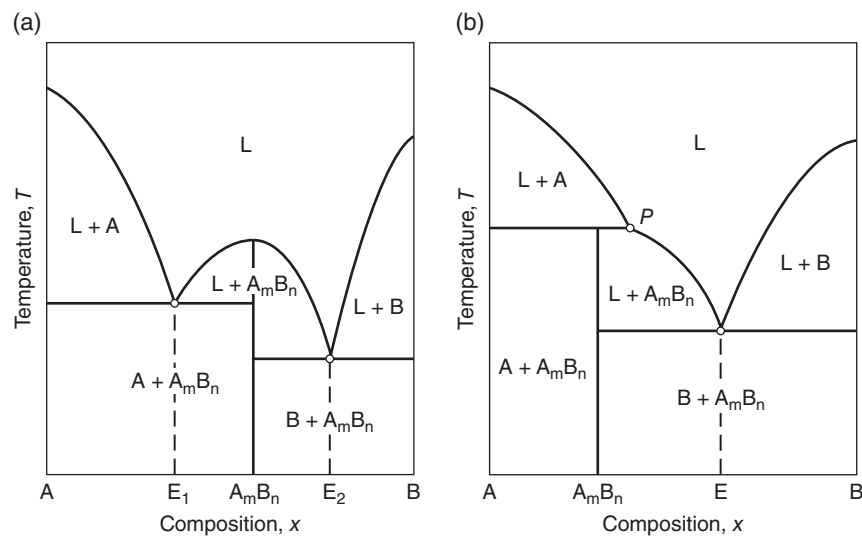


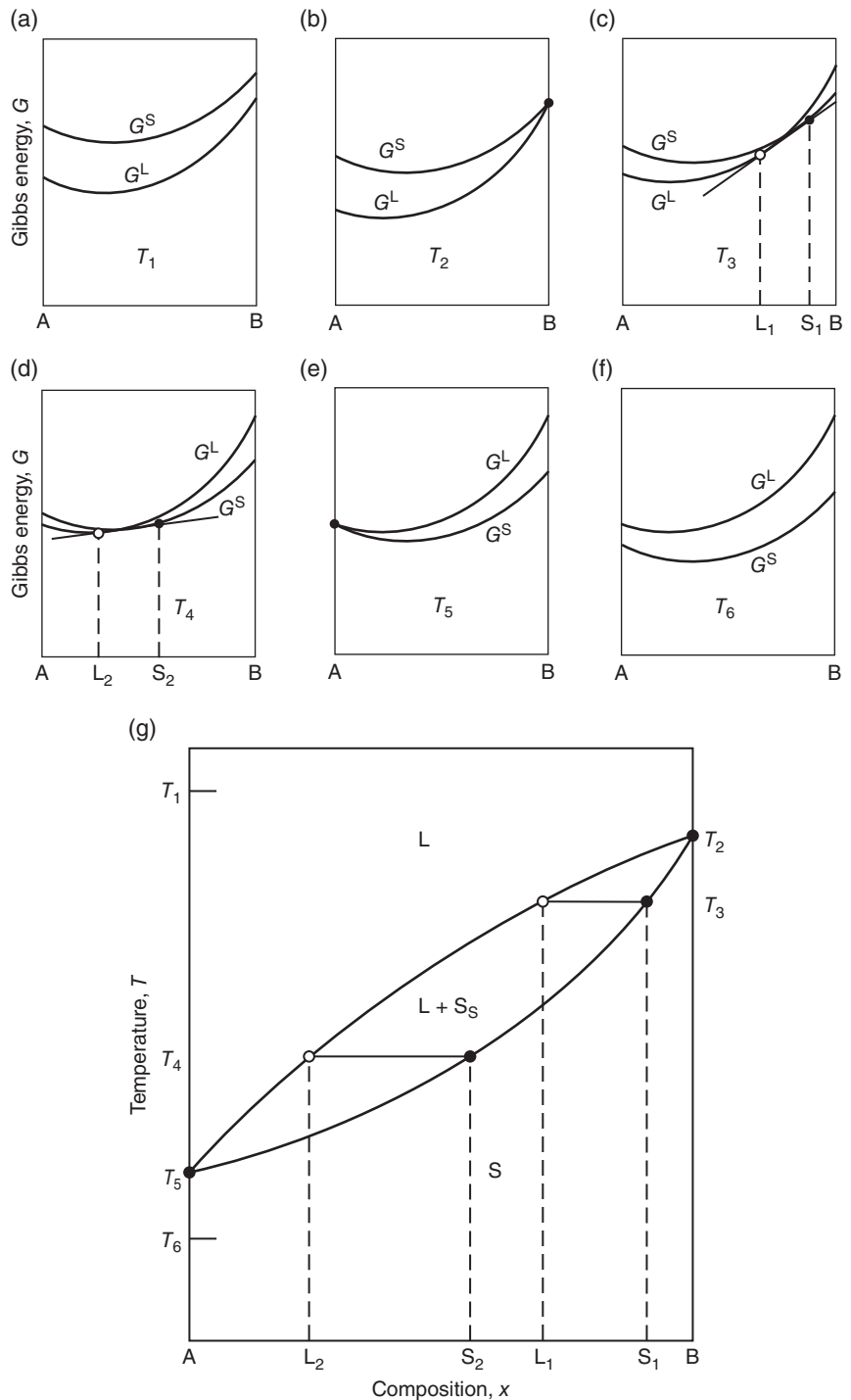
Figure 3 Transformation of a two-eutectic system (a) into a peritectic system with a single eutectic (b) resulting from the incongruent melting of the intermediate compound A_mB_n (peritectic point P).

3.4 Complete Miscibility in Melt and Solid Solution

In case of complete miscibility between the components A and B in both liquid and solid states, the Gibbs energies of the binary melt (G^L) and solid solution (G^S) plot as concave curves in G - x coordinates. The changes of the relative positions of the curves with temperature are

illustrated by a series of G - x diagrams in Figure 4 from the highest temperature T_1 where the melt is stable in the whole range of compositions (Figure 4a) to T_6 where the solid solution is the single stable phase (Figure 4f). At intermediate temperatures T_2 - T_5 , the melt and solid solution coexist, and the equilibrium compositions of the liquid and solid phases L and S are defined by

Figure 4 Binary system with complete miscibility in both the solid and molten phases. (a-f) Gibbs free energies against composition at six decreasing temperatures. (g) Derived spindle-type phase diagram.



intersections of the curves G^L and G^S with a common tangent line (Figure 4c and d). The resulting T - x phase diagram features convex liquidus and concave solidus curves intersecting at the melting points of the pure components A and B (Figure 4b and g). But the $L + A_{ss}$ (or B_{ss}) two-phase fields of the solid solutions (ss) may have a more complex V shape and consist of two or even more segments (Figure 5b).

3.5 Complete Miscibility in Melt and Limited Miscibility in Solid Solution

If the enthalpy of mixing of the A-B solid solution is positive, the Gibbs free energy of the solid solution changes with falling temperature in the way illustrated in Figure 1 so, below the critical temperature T_c , the homogeneous binary solid solution splits in two coexisting solid subsolutions A_{ss} and B_{ss} . The equilibrium compositions of the phases in T - x coordinates plot along

the bell-shaped convex curve labeled as the binodal in Figure 1b (which is actually termed *solvus* for solid solutions).

Four basic topological types of T - x binary diagrams with limited miscibility in solid solution are presented in Figure 5. The differences lie in the shape of the liquidus curve and relationships between solidus and solvus. The liquidus curve slopes in one direction and has no inflection in Figure 4a and c, whereas the curve is V shaped in Figure 5b and d. The solvus and solidus do not intersect in Figure 5a and b, whereas they do so in Figure 5c and d. In Figure 5a and b, the melt crystallizes to the homogeneous solid solution S_s , which unmixes to the subsolutions S_{s1} and S_{s2} at lower temperatures. In Figure 5c and d the homogeneous solid solution does not exist at subsolidus temperatures. The phase relationships in solid solutions can be very complex, but they are relevant to glass-making only for production of glass ceramics, where they are critical to achieve the desired properties (Chapters 7.11 and 8.5).

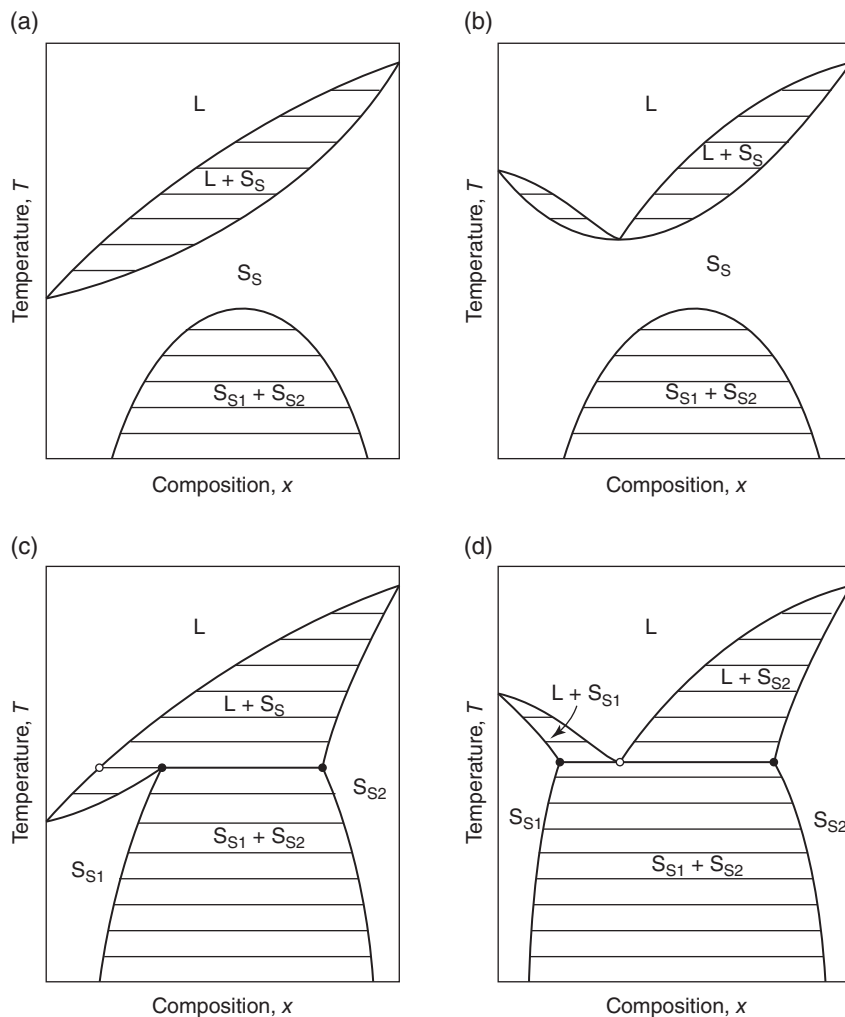


Figure 5 From (a) to (d), the transformation of a spindle-type into a eutectic system with limited solid solution upon increasing mutual solubility of the two components in the solid state, causing the solvus to intersect the solidus and liquidus curves and invariant eutectic points to appear, between which the solidus becomes isothermal.

3.6 Limited Miscibility in Melt

Two alternative types of topological relationships between liquid immiscibility (binodal) and crystallization (liquidus) in a binary system are illustrated in Figure 6. In Figure 6a, the consolute temperature of the binodal curve is above the liquidus, so the binodal and liquidus curves intersect. In a binary isobaric system, the equilibrium of immiscible liquids L_1 and L_2 with a solid phase is invariant. Therefore, the immiscible liquids must be in equilibrium with one and the same solid (B in Figure 6a) so that the two intersection points of the binodal and solidus curves are at the same temperature. The binodal curve represents stable univariant two-liquid equilibrium above the liquidus, but its extension below the liquidus is metastable (dashed line in Figure 6a). Alternatively, the consolute temperature and the whole binodal curve may lie below the liquidus and thus refer to a metastable state (Figure 6b). In this case, the liquidus segment above the metastable binodal is usually flattened and exhibits a characteristic sigmoidal shape.

Many metal oxides have limited solubility in typical silicate, borate, and other glass-forming melts, and liquid miscibility gaps are common in glass-forming systems. Glassmaking is often affected by both stable and metastable immiscibility or phase separation as it is usually called in technological literature [4, 5]. When a homogeneous melt in the compositional region of metastable liquid immiscibility is rapidly cooled from superliquidus temperatures, it may not crystallize for kinetic reasons, but the undercooled liquid may unmix when it gets below the metastable continuation of the binodal. The resulting emulsion is usually very fine, often submicron, and

quenches to turbid, opalescent glass. Another way to achieve metastable unmixing is to anneal an initially homogeneous glass at temperatures above the glass transition but below the metastable binodal.

4 Ternary Diagrams

With the addition of one more component as an independent variable, T - x diagrams become three-dimensional. The conventional form of these diagrams is that of a trigonal prism whose base is the plane of barycentric compositional coordinates and vertical axis is the temperature scale (Figure 7a). In three dimensions, two-phase liquidus equilibria plot along curved liquidus planes; the assemblages of liquid and two solid phases are univariant and plot along three-dimensional curves; four-phase equilibria, such as ternary eutectic E_{ABC} in Figure 7, are plotted as points. For convenience, ternary diagrams are usually presented not in three-dimensional form but as projections of topological elements, planes, curves, and points, on the basal compositional plane (Figure 7b). As in topographic maps, elevations along the temperature axis are traced by isothermal lines, and down-temperature directions along univariant curves are commonly indicated by arrows.

With an increasing number of components, the basic types of phase equilibria remain the same, so ternary diagrams can be viewed as various combinations of topologic relationships outlined in Section 3. Ternary diagrams may comprise binary and ternary compounds, solid solutions, and liquid miscibility gaps. For example, a hypothetical isobaric ternary phase diagram in Figure 8

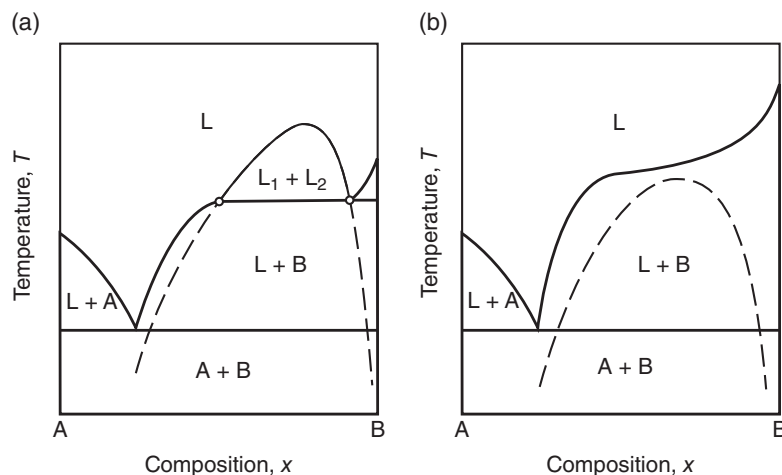


Figure 6 Effect of the extent of liquid unmixing on the topology of a binary eutectic system. (a) Stable unmixing above the liquidus, intersecting at L_2 the small liquidus branch of the B component limited by the L_1 - L_2 tie line, below which it extends metastably. (b) Metastable unmixing below the liquidus, which generally shows an inflexion point near the critical composition of the solvus.

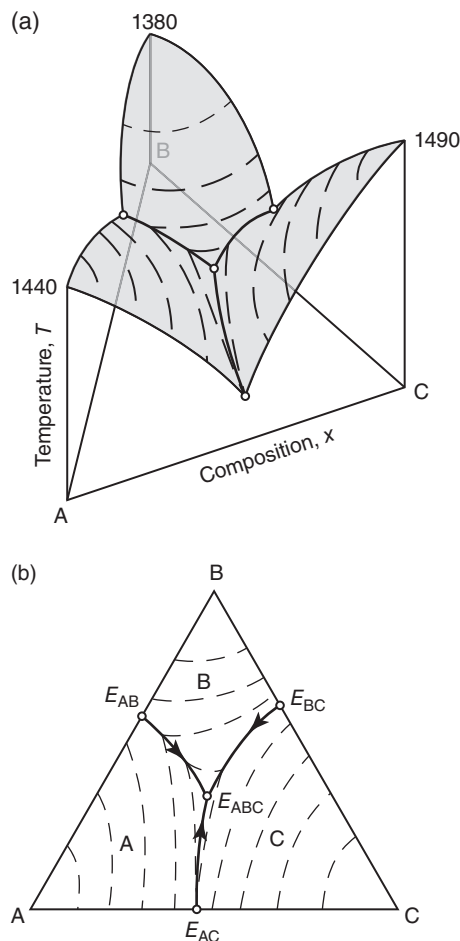


Figure 7 Eutectic phase diagram of a ternary system A–B–C. (a) Three-dimensional representation: the cotectic lines beginning from the binary eutectics (E_{AB} , E_{AC} , E_{BC}) to converge at the lower temperature of the ternary eutectic (E_{ABC}). (b) Projection of (a) along the temperature axis. Isotherms shown as dashed lines.

features congruently melting binary and ternary compounds BC and A_2BC_2 and incongruently melting compounds B_4C and A_2B_3C . There are four invariant ternary eutectic and three invariant ternary peritectic points corresponding to the following reactions:

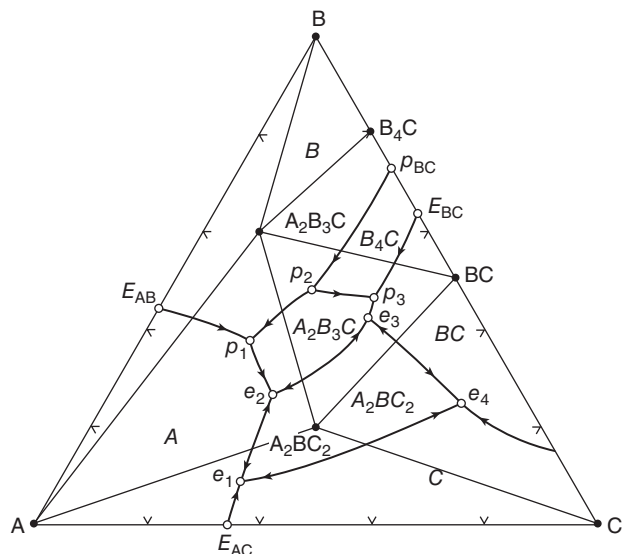
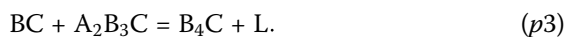
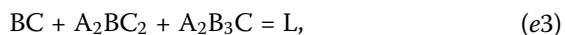
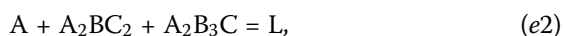


Figure 8 Phase diagram of a hypothetical ternary system with congruently and incongruently melting binary and ternary compounds. See text for discussion.

Stably coexisting solids are connected in Figure 8 by *tie lines*. Notably, the compositions of compounds plot within the primary crystallization fields when melting is congruent, but in the primary crystallization fields of some other phases when it is incongruent.

5 Some Phase Diagrams for Glass-Forming Systems

5.1 The Determining Influence of Cation Size and Charge

Typical glass-forming melts are mixtures of molten oxides with strong chemical interactions and covalent or ionic bonds between metal cations and the oxyanion O^{2-} . Metal cations in glass-forming systems are traditionally classified in two major groups, namely, network formers and network modifiers (Chapters 2.1 and 2.4). Network formers are small, highly charged cations with coordination numbers not greater than 4 and strong covalent bonds to O^{2-} . Fourfold coordinated Si^{4+} is the most common and important network former, but the group of typical network formers in natural and technological glasses also includes P^{5+} , B^{3+} , Ge^{4+} , Sb^{3+} , and As^{3+} . Network-modifying cations have ionic radii greater than 87.2 pm [6] and coordination numbers equal to or higher than 5 [7]. The group comprises alkali and alkaline earth cations (excluding Li^+ , Be^{2+} , and Mg^{2+}), rare earth cations, Th^{4+} , and U^{4+} . Cations with ionic radii greater than that of Si^{4+} (26 pm) but smaller than 87.2 pm belong

to the intermediate, amphoteric group. According to spectroscopic studies, amphoteric cations have at least two coordination numbers. One coordination number is 4 and another one is usually 5 or 6. The most important amphoteric cation in natural and technological glasses is Al^{3+} , but the group also includes Li^+ , Be^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , Sc^{3+} , Ga^{3+} , Ti^{4+} , Zr^{4+} , Hf^{4+} , Nb^{5+} , Ta^{5+} , and some other high field strength cations.

This importance of ionic radii stems from the fact that, as a first approximation, bonding can be considered to be primarily ionic in oxide systems. Notwithstanding the aforementioned role of Si speciation, element mixing then is determined by similarities in electric charges and ionic radii. In purely oxide systems, oxygen is the sole anion present so only cation mixing needs to be dealt with. For the same nominal charges, Na^+ (116 pm), for instance, readily substitutes for K^+ (138 pm) and Mg^{2+} (72 pm) for Fe^{2+} (78 pm) or Ni^{2+} (69 pm) but less so for Ca^{2+} (100 pm). When the electrical charges differ, substitution is nonetheless possible provided that a *charge-compensating* cation is also exchanged, as illustrated by the well-known coupled substitutions of Na^+ and Al^{3+} for Si^{4+} .

A selection of phase diagrams will now illustrate the fundamental link between the ionic characteristics of the metals (the nominal charge Z , ionic radius r , and ionic potential Z/r) and the phase equilibria between their oxides in the processes of melting, crystallization and glass formation. These examples are limited to the simplest and the most widely used glass-forming systems for technology and research.

5.2 Silica–Metal Oxide Binaries

Binary systems of silica with alkali and alkaline earth oxides (Figure 9) share common topological features, which include the occurrence of stable or metastable liquid immiscibility at high silica content and eutectic-type relationships between multiple congruently and incongruently melting binary compounds at high concentrations of metal oxides. The stability of intermediate compounds and the size of liquid miscibility gap systematically change with the nominal charge Z and radius r of the metal cation, a feature indicating that interactions between the components are actually predominantly Coulombic in nature.

Regarding the stability of intermediate compounds, a general trend apparent in Figure 9 is that the composition of the most silica-rich compound shifts toward that of the metal oxide with increasing ionic potential Z/r of the metal cation. Whereas potassium tetrasilicate $\text{K}_2\text{Si}_4\text{O}_9$ with 80 mol % SiO_2 is stable in the K_2O – SiO_2 system, the most silica-rich compound in the other binary systems presented in Figure 9 are $\text{Na}_6\text{Si}_8\text{O}_{19}$ (73 mol % SiO_2), $\text{Li}_2\text{Si}_2\text{O}_5$

and $\text{Ba}_2\text{Si}_2\text{O}_5$ (67 mol % SiO_2), and CaSiO_3 and MgSiO_3 (50 mol % SiO_2). The stability of the silica-poor compounds with SiO_2 molar concentrations below 50 % also tends to increase with increasing Z/r .

The liquidus temperatures of the compounds are, however, more important for glassmaking than the compositions of intermediate compounds. Here the contrast between alkali and alkaline earth systems is dramatic, the liquidus temperatures being systematically lower for the former than for the latter. The differences are especially large at the lowest eutectic points, which are below 800 °C in K and Na binaries and above 1300 °C in alkaline earth systems. The low melting temperature of alkali silicates is one of the reasons why the first, most ancient artificial glasses were close to eutectic compositions in the Na_2O – SiO_2 system.

Liquid immiscibility is another major obstacle for glassmaking. Good correlation between the size of miscibility gaps in binary metal oxide–silica systems and Coulombic properties of the metal cations such as Z/r has been noticed ever since the pioneering studies by Greig [1]. To rationalize the correlation, Hess [17, 18] proposed that the forces responsible for melt unmixing at the atomic level are Coulombic and repulsive in nature. He pointed out that network-modifying cations are surrounded in silicate melts by both bridging and nonbridging oxyanions. Oxygen ions in bridging ($\text{Si}-\text{O}-\text{Si}$) and nonbridging positions ($\text{Si}-\text{O}-\text{M}$, where M is a network-modifying cation) isolate the network-modifying cations from one another by providing screens that mask the positive charges. However, modifier cations that are partly or wholly coordinated by bridging oxygen are poorly shielded from one another because the bridging oxygen ions are bonded to Si^{4+} cations by strong covalent bonds. Consequently, significant Coulombic repulsions build up between network-modifying cations, which may eventually result in phase separation through melt unmixing. The higher the ionic potential of modifier cations, the greater the Coulombic repulsions between them, and the larger the width of the resulting miscibility gap.

In a detailed analysis of binary systems, Hudon and Baker [7, 19, 20] noticed that the relationships between the ionic potential of network-modifying cations and the size of miscibility gaps are not linear. Furthermore, each group of homovalent cations (cations with the same Z) forms its own trend (Figure 10). For each group, the compositional width of miscibility gap and the unmixing temperature increase with Z/r reach a maximum and then decrease. The maximum is reached at $r = 87.2$ pm, which, as mentioned above, defines the transition from true network modifiers to amphoteric cations. Hudon and Baker assumed the existence of structural control on immiscibility in which the cation radius appears to have an important role. To rationalize the convex trends,

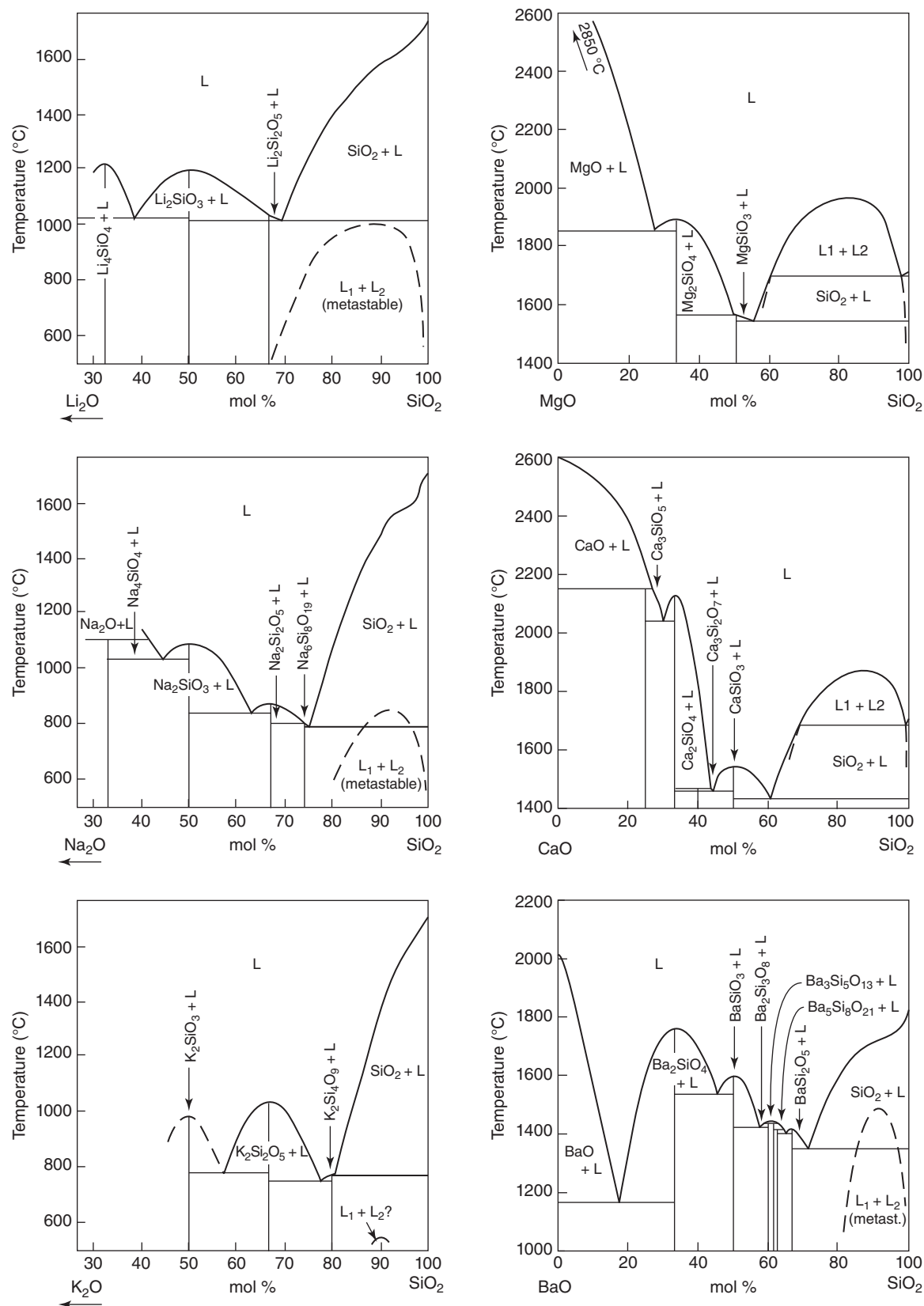


Figure 9 Phase equilibria in binary silica-metal oxide systems. Data for Li₂O [8], Na₂O [9, 10], K₂O [11], MgO [12], CaO [13, 14], and BaO [15]. Liquid miscibility gaps according to [7] and references therein. Source: Redrawn from [16], simplified.

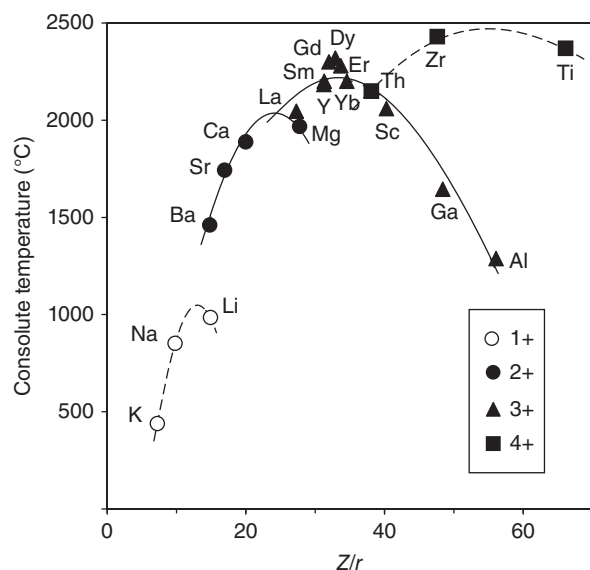


Figure 10 Maxima in the critical temperatures of liquid miscibility in metal oxide–silica binaries when plotted against the ionic potential of the metal ion Z/r after [7]. Ionic radii r in nanometers [6]. Parabolic curves visually fitted to the points for homovalent cations.

they pointed out the increasing degree of covalency of the M–O bonds in homovalent groups of elements with decreasing r . Therefore, amphoteric cations capable of fourfold coordination seem to undergo weak or no Coulombic repulsion and tend to produce little or no phase separation.

Liquid miscibility gaps in complex multicomponent silicate melts tend to expand with additions of even small amounts of Fe, Ti, and P. The effects of Fe because of its high natural abundance are of special importance for immiscibility in natural magmatic melts. An anomalously low solubility of Fe ions in silicate melts appears to result from characteristic features of electron shells. Cations of transition elements from the first row in the periodic table, such as Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , V^{3+} , and Cr^{3+} , have five d-electron orbitals, which poorly shield atomic nuclei [7, 19]. Notably, miscibility gaps associated with the divalent cations in corresponding oxide–silica binaries are larger than expected from the general Z/r trend, and immiscibility gaps are even greater in binaries of trivalent Cr^{3+} , V^{3+} , and Fe^{3+} [7, 19].

5.3 The System Na_2O – CaO – SiO_2

Soda-lime silicates are of prime technological importance not only for the glass industry but also for the production of Na–Ca glass ceramics and Portland cement. The system comprises numerous binary and ternary compounds and invariant eutectic and peritectic points (Figure 11).

The compositions of the most common commercial glasses such as window and container glasses lie close to the ternary eutectic O at 725 °C (Figure 11) in the primary crystallization field of the ternary phase devitrite $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$. As indicated by its name, this phase is the principal devitrification product of commercial soda-lime-silica glasses. It represents a typical example of an incongruently melting phase since it decomposes at 1060 °C into Ca metasilicate (CaSiO_3) and a 20 Na_2O •15 CaO •65 SiO_2 (wt %) liquid.

The consolute temperature of the liquid immiscibility dome, which is well above 1800 °C in the boundary system CaO – SiO_2 , rapidly decreases upon addition of Na_2O . The immiscibility dome eventually dives below the liquidus of silica polymorphs and becomes metastable at Na_2O concentrations of only 3 wt %. Metastable immiscibility extends to the compositions of commercial glasses for which evidence of phase separation has been found by electron microscope analyses of carefully etched samples [5].

5.4 Borosilicate Systems

Sodium borosilicate glasses are characterized by lower thermal expansion coefficients, better chemical durability, higher dielectric strengths, and higher softening temperatures than comparable soda-lime-silica glasses (Chapter 7.6). These advantages are reflected by the great variety of their consumer and technological applications. The ternary phase diagram Na_2O – B_2O_3 – SiO_2 (Figure 12) contains information fundamental for manufacturing of borosilicate glasses.

Although the limiting systems Na_2O – B_2O_3 and Na_2O – SiO_2 comprise numerous binary compounds, no ternary compound appears on the liquidus of the ternary system, in accordance with the lack of intermediate compounds in the B_2O_3 – SiO_2 system. The network formers B_2O_3 and SiO_2 have eutectic-type melting relationships, where the eutectic point strongly shifts toward the low-melting B_2O_3 . Binary mixtures of boron oxide and silica show strong tendency to metastable immiscibility in a broad compositional range below the liquidus of silica polymorphs. Compositions of commercial sodium borosilicate glasses lie in the silica primary crystallization field where liquidus temperatures drop below 1100 °C (Figure 12).

6 Perspectives

As a result of the systematic efforts made for more than a century, by far phase diagrams remain the most extensive source of thermodynamic information available for oxide

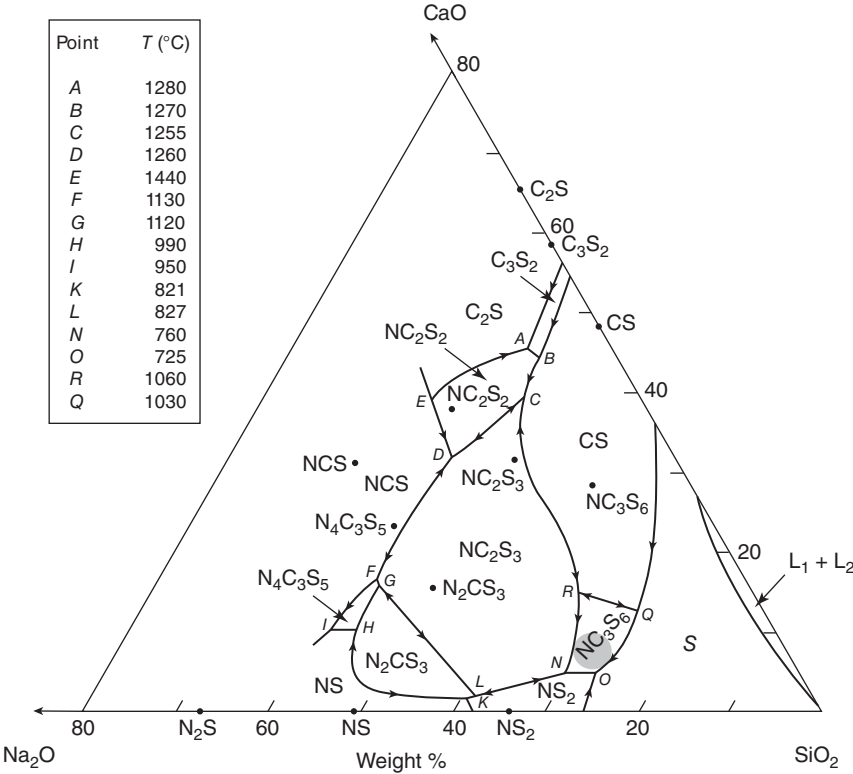


Figure 11 Phase diagram of the ternary system Na_2O – CaO – SiO_2 [21–24]; numbers are in mol %. Field of stable liquid immiscibility indicated as $L_1 + L_2$. Ternary eutectic and peritectic points labeled by capital Latin letters, with temperatures listed in the table. Typical compositions of commercial glasses shown by the gray oval field.

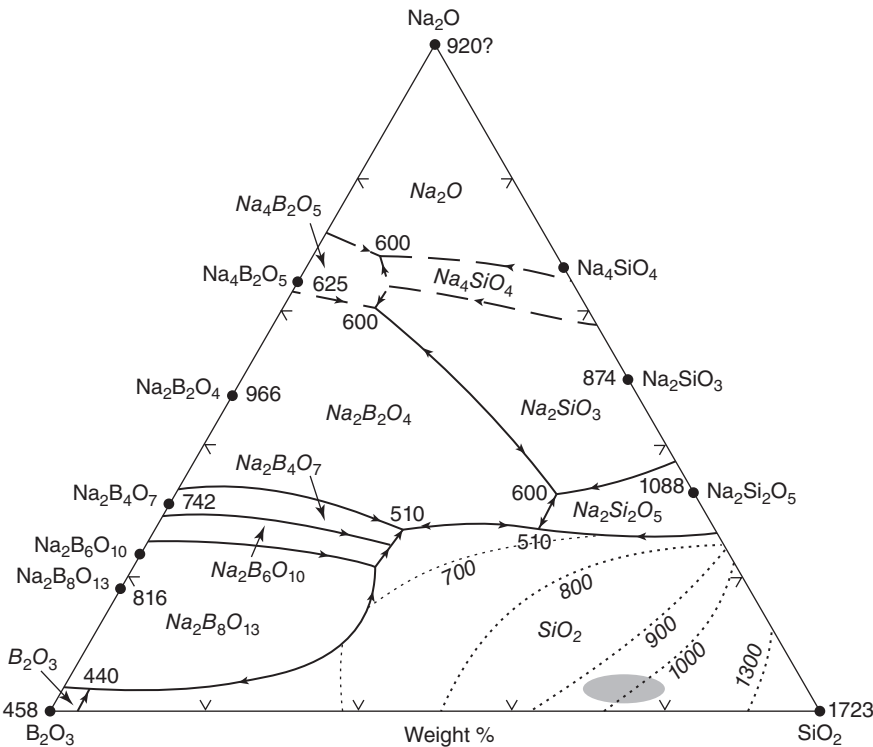


Figure 12 Phase diagram of the ternary system Na_2O – B_2O_3 – SiO_2 [25]. Melting temperatures of binary compounds and temperatures of key invariant points in degrees Celsius. Isotherms in the silica crystallization field indicated by dotted lines. Typical compositions of commercial glasses shown by the gray oval field.

materials. Hence, they constitute the main basis on which analyses are in turn performed to set up thermodynamic models with which not only phase equilibria but also oxide activities and other relevant parameters can be predicted for very wide compositional ranges (Chapter 5.3). Compared to phase equilibria experiments, calculations have of course tremendous advantages in terms of cost and rapidity, so efforts are actively pursued to improve their accuracy and reliability. It should be kept in mind, however, that most phase diagrams have been determined from optical observations of quenched samples at times when modern microanalytical methods (Chapter 2.2) were not existing. As a result, it is likely that many diagrams considered as eutectic would actually exhibit limited solid solutions, as has been shown in the important system $\text{SiO}_2\text{--CaAl}_2\text{Si}_2\text{O}_8$ by the presence of an excess SiO_2 in the anorthite structure [26]. Although it is unlikely that even the most important phase diagrams will be redetermined with the added benefit of microanalyses, such limitations of the available data should not be overlooked in current and future theoretical work.

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5.3

Thermodynamic Models of Oxide Melts

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1 Introduction

When prepared by the usual melting process, glasses have of course melts as *precursors*. Their lack of long-range order then reflects that of the melt frozen in at the glass transition if the rate of heat loss on cooling is high enough with respect to the rate of the structural rearrangements that would lead to the crystalline phases. Although prediction of kinetic factors such as minimum cooling rates for vitrification is beyond the scope of equilibrium thermodynamics, thermodynamic models of melts are important for glass makers, metallurgists, and earth scientist. Because these models are devised to predict equilibrium conditions of melts with crystalline or vapor phases (Chapter 5.2), they may be used either to determine the appropriate melting conditions of glasses and slags or to reconstruct the history of igneous rocks. In this respect, temperature is not the only intensive parameter to be dealt with. The partial pressures of volatiles, redox conditions, and pressure (in earth sciences) have also to be considered as they can greatly affect phase equilibria or physical properties of glasses such as color (Chapter 6.2).

At a given temperature (T) and pressure (P), the equilibrium state of a system is determined by the minimum of its Gibbs free energy

$$G = H - TS, \quad (1)$$

where H is enthalpy and S entropy. A thermodynamic model thus relates the enthalpy and entropy of a system to its temperature, pressure (if needed), and composition (x) so as to make possible to find the minimum of G under the conditions of interest. Any thermodynamic model is in fact based on two different kinds of assumptions. The

first deals with the set of components in terms of which the chemical composition of the system is expressed, the second with the formal relationships with which the mole fractions of the selected components are mutually related in the used enthalpy and entropy expressions.

From the outset we will emphasize that a component (i.e. a “stoichiometric entity” represented by a group of atoms) on which is resting any phenomenological thermodynamic theory of mixed phases may be suggestive of certain structural features. But if such features represent a potential advantage, they are certainly not a foundation on which the theory rests. Moreover, a major problem encountered for oxide melts is that they are *associated liquids*, i.e. they have a complex structure that is continuously rearranged and in which the relevant molecular species are short lived and, thus, not readily identified. This is the reason why melt components have been defined in many different ways in the literature. The simple system $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ (olivine in the crystalline state) may, for instance, be considered as composed of Fe_2SiO_4 (fayalite) and Mg_2SiO_4 (forsterite), of oxides (MgO ; FeO ; SiO_2), of elements (Mg ; Fe ; O), or of ions (Mg^{2+} , Fe^{2+} ; O^{2-}), the only requirement being that the number of components be consistent with the phase rule. Correlatively, analytical expressions used for G also show wide differences. As exemplified in silicates by the change from the three-dimensional network of SiO_4^{4-} tetrahedra of pure SiO_2 to the isolated SiO_4^{4-} units of SiO_2 -poor systems (Chapter 2.4), the structure of a melt can in addition change so much with composition that large differences can be found between the approaches followed by metallurgists interested in compositionally simple SiO_2 -poor slags and by glass scientists and geochemists focusing on complex SiO_2 -rich melts.

As a result, there is at this moment no single thermodynamic model with which phase equilibria can be calculated for any kind of oxide melts. Although it is clearly beyond

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the scope of this chapter to review the large diversity of models proposed in the literature, most of them can be grouped into one of the four classes that can be termed (i) fictive-chemical, (ii) fictive-structural, (iii) quasi-chemical, and (iv) polymeric. As it will be discussed here, the philosophy beyond each one of the four classes is basically different, so all models have their own advantages and drawbacks, with the consequence that their uses are generally restricted to specific ranges of composition under limited temperature and pressure intervals.

2 General Considerations

2.1 Gibbs Free Energy Minimization Principle and Mixing Properties

In depicting the mixing properties of a multicomponent liquid, it is convenient to adopt a *mixture* notation with which all components in mixture usually have as a standard state the pure component at the T and P of interest. In an ideal mixture there are no interactions between individual components, so the enthalpy of mixing (ΔH_{mix}) is zero. But mixing between n components in a mixture necessarily causes an increase of entropy. For ideal (i.e. random) mixing, this increase is given by

$$\Delta S_{\text{mix,id}} = -R \sum_{i=1}^n x_i \ln x_i, \quad (2)$$

where x_i is the mol fraction of the i th component. As a net result, the chemical potential of the i th component in the ideal mixture at P and T simply varies with composition according to

$$\mu_{i,P,T} = \mu_{i,P,T}^0 + RT \ln x_{i,P,T}, \quad (3)$$

where $\mu_{i,P,T}^0$ is the standard state potential at the P , T of interest. In condensed phases in general, and oxide crystals and melts in particular, mixing is not ideal because species interact more or less strongly and, as a consequence, are not randomly mixed. The relation with the standard state potential is then depicted in terms of the *thermodynamic activity* $a_{i,P,T}$:

$$\begin{aligned} \mu_{i,P,T} &= \mu_{i,P,T}^0 + RT \ln a_{i,P,T} = \mu_{i,P,T}^0 + RT \ln x_{i,P,T} \\ &\quad + RT \ln \gamma_{i,P,T}. \end{aligned} \quad (4)$$

where $\gamma_{i,P,T}$ is the activity coefficient.

The Gibbs free energy of the system is related to the chemical potential μ of the various components in the system and their number of moles n by

$$G_{(P,T,x)} = \sum_{i=1}^n n_i \mu_{i,P,T}. \quad (5)$$

With this definition, it follows from the Gibbs free energy minimization principle that another criterion for equilibrium in a multiphase system is that the chemical potential of any component be the same in all coexisting ($\alpha, \beta, \dots, \epsilon$) phases:

$$\mu_{i,P,T,\alpha} = \mu_{i,P,T,\beta} = \dots = \mu_{i,P,T,\epsilon}. \quad (6)$$

Finally, the temperatures at which crystal–liquid (or vapor–liquid) equilibria take place in solutions are not fixed. Thus, for each phase involved, the variations with temperature of the enthalpy and entropy terms must be calculated with the relevant heat capacity data. For example, at a given temperature T , the standard state enthalpy and entropy of the liquid and crystal components at T of reference (T_{ref}) are related by

$$H_{i,l}^0 = H_{i,c}^0 + \int_{T_{\text{ref}}}^{T_{\text{fus}}} C_{P,i,c} dT + H_{\text{fus}}^0 - \int_{T_{\text{ref}}}^{T_{\text{fus}}} C_{P,i,l} dT, \quad (7)$$

$$S_{i,l}^0 = S_{i,c}^0 + \int_{T_{\text{ref}}}^{T_{\text{fus}}} \frac{C_{P,i,c}}{T} dT + \frac{H_{\text{fus}}^0}{T_{\text{fus}}} - \int_{T_{\text{ref}}}^{T_{\text{fus}}} \frac{C_{P,i,l}}{T} dT, \quad (8)$$

where H_{fus}^0 is the enthalpy of fusion at the reversible temperature of fusion (T_{fus}) of the component. In other words, phase equilibrium calculations rely on extensive thermochemical information for all the phases considered. In this respect the enthalpies of fusion (or vaporization) and also the high-temperature heat capacities for the molten and crystalline (or vapor) phases are critical, especially when dealing with large freezing-point depressions that can attain, as in alkali-silica systems, more than 900 K. A summary of available data is found in Chapter 3.6.

Crystals in oxide systems are generally themselves solid mixtures. At least for minerals of geochemical interest, however, good thermodynamic models have already been set up and are thus ready to be used. In the case of melts, whereas there is no method to measure directly entropies of mixing, enthalpies of mixing can be determined calorimetrically. Unfortunately, these measurements are available for very few systems because they are time-consuming and beset by significant experimental uncertainties (Chapter 3.6).

It follows that the data employed to calibrate thermodynamic models of oxide melts are mainly experimentally determined phase diagrams. Most of them have been established between 1920 and 1960 from optical examination of samples quenched from given temperatures

and pressures. Although the liquidus and solidus temperatures bracketed in this manner are usually accurate to within a few degrees at room pressure, these determinations were made before the advent of chemical microanalyses, so crystals were assumed to be stoichiometric, and limited solid solutions could not be detected. Both assumptions introduce uncertainties in derived Gibbs free energies that should not be overlooked, although their evaluation is not easy.

2.2 A First Example: Melting in the CaO–SiO₂ System

As a real example, consider the equilibrium between a melt of a certain composition x along the *liquidus*, i.e. the P, T, x hypersurface separating the pure melt from the melt + crystal regions (Chapter 5.2). For this purpose we have selected the G – x relationship for the binary system CaO–SiO₂ at $P = 10^5$ Pa (i.e. 1 bar), first at $T = 1773.15$ K (hereafter noted as 1773 K) (Figure 1) and then in a wider temperature range (Figure 2). In addition to lime (CaO) and the β -quartz and β -cristobalite polymorphs of SiO₂, seven other compounds are found along the liquidus: hatrurite (Ca₃SiO₅), two polymorphs of Ca₂SiO₄ (α -larnite and bredigite), rankinite (Ca₃Si₂O₇),

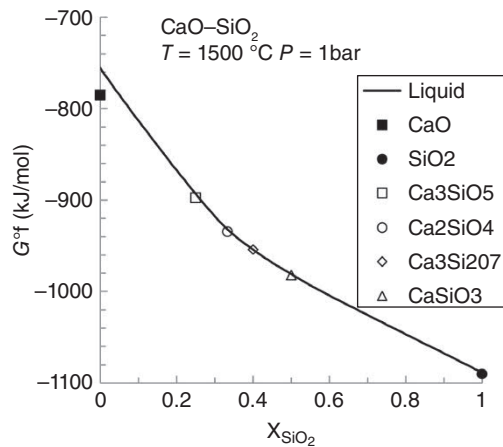


Figure 1 Gibbs free energy of formation from the elements at the standard state of CaO–SiO₂ liquids (solid line) and of the precipitating crystal (symbols) on a 1 mol oxide basis (e.g. Ca₃SiO₅ $\Rightarrow$ Ca_{0.75}Si_{0.25}O_{1.25} etc.). Liquid computed with a hybrid polymeric approach [1, 2] adopting for the chemical interaction (G_{chem}) a T -dependent polymerization constant, $\ln K_p = -14939/T + 0.17$, and for the strain energy (G_{strain}) a subregular expansion operating on the SiO₂-rich side of the system, $f(x) = -1.2 \times (1 - 2x_{\text{SiO}_2}) - 8 \times (1 - 2x_{\text{SiO}_2})^6$; $x_{\text{SiO}_2} \geq 0.5$. The bulk Gibbs free energy of mixing is weighted with the number of contacts between oxygen quasi-species (see Eq. 44), i.e. $G_{\text{mixing}} = \frac{(O^-)}{2} \times [RT \ln K_p + f(x)]$. See Ref. [2] for the sources of thermodynamic data concerning the crystalline phases.

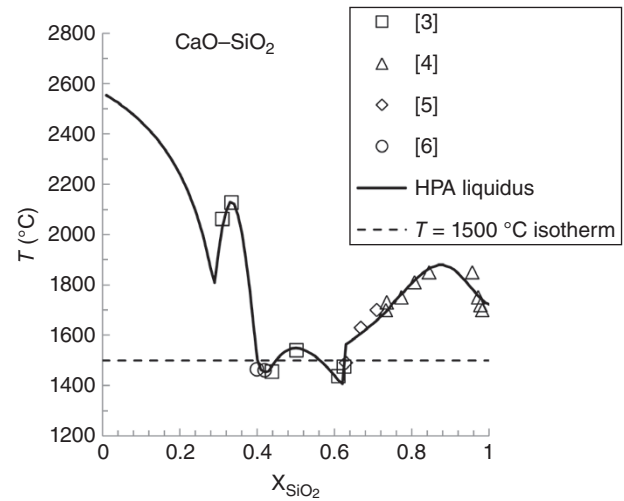


Figure 2 Room-pressure liquidus of the CaO–SiO₂ system derived from the hybrid polymeric approach (solid line) and from observations (symbols).

and two polymorphs of CaSiO₃ (α -wollastonite and β pseudo-wollastonite).

The Gibbs free energies of formation of all these stoichiometric crystals are known at the temperature and pressure of interest from thermochemical measurements. To these values we have superimposed in Figure 1 the Gibbs free energies of formation of the liquids under the same conditions based on a simple polymeric model [1, 2]. This Gibbs free energy curve is generally concave upward and almost touches the Gibbs free energy points of the various solids, pointing to complete miscibility over a wide compositional range except at high silica content where the flatness of the $G = f(x)$ curve indicates a limited liquid immiscibility domain.

Either by minimizing G or by applying the equilibrium criterion (6), one finds that pseudo-wollastonite, α -larnite, and β -cristobalite coexist stably with melts whose SiO₂ mol fractions are 0.45 and 0.56 and 0.40 and 0.625, respectively. Repeating this exercise at various temperatures to collect the points of stable coexistence, one builds a isobaric phase diagram, i.e. a so-called Schreinemaker's projection of chemical potentials onto the T, x space at constant P , which delineates the stability fields of the various phases (Figure 2). In agreement with experimental observations [3], the calculations indicate that pseudo-wollastonite melts congruently at 1550 °C and forms a thermal barrier because initial liquids with SiO₂ mol fractions higher and lower than 0.5 become progressively more SiO₂ rich and more SiO₂ poor, respectively, when crystallization proceeds.

A detailed first-principles computation of the Gibbs free energy of crystalline CaSiO₃ at 1773 K yields a bulk energy of ~ 1177 hartree per mol of oxides, corresponding

to $\sim 3.09 \times 10^6$ kJ/mol [1 hartree = $\hbar^2/(m_e a_0)$ with $\hbar$ = reduced Planck's constant, m_e = mass of electron at rest, and a_0 = Bohr radius]. On the other hand, the Gibbs free energy of formation from the elements at 1773 K and 1 bar are -981.3 and -981.7 kJ/mol for the α - and β -phases of CaSiO_3 , whereas that of the liquid is -981.0 kJ/mol (-922.2 kJ arising from the simple summation of the chemical potentials of the pure CaO and SiO_2 liquid components and -58.8 kJ arising from mixing contributions). The overall net ΔG between the crystalline and the liquid states is about 0.7 kJ/mol, which indicates that the influence of the aggregation state of CaSiO_3 on the bulk energy of the substance is only ~ 226 ppb. This simple calculation stresses how much the calculated topology of a phase diagram may be affected by slight errors in the input thermochemical data (or in the mixing model).

3 Thermodynamic Models

3.1 Fictive-Chemical Models: Regular Mixtures

The purpose of this class of models is not to yield even an approximate physical explanation of the observed mixing properties of the phases but, rather, to account for them empirically through simple polynomial expansions of the excess Gibbs free energies of mixing. It is in fact this lack of concern for fundamental aspects that makes these models so useful, especially for chemically complex systems where many binary interactions cancel out to a large extent.

To this class belongs the mixing models developed by Ghiorso and coworkers [7] for the composition range of natural magmas with the *ad hoc* components listed in Table 1, whose choice was dictated by simple convenience, i.e. by the possibility of deriving realistic thermodynamic data for melt constituents through either empirical procedures or univariant equilibria involving their crystalline counterparts. Because all components have the same standard state (pure melt at the T , P of interest) and the interaction parameters do not vary with temperature, the model may be ascribed to a regular mixture of the zeroth principle (complete configurational disorder):

$$G_{\text{melt},P,T} = \sum_i n_i \mu_i^0 + RT \sum_i n_i \ln x_i + \frac{1}{2} n_{\text{total}} \sum_i \sum_j W_{ij} x_i x_j. \quad (9)$$

The first step in the model is a normative calculation to establish the molar amounts of the various melt components (Table 1). With 15 such components, one should know 120 W_{ij} parameters to describe all binary interactions. But application of inverse methods to the plethora of petrogenetic observations in natural systems shows

Table 1 Melt components in the Ghiorso–Carmichael model and calculation of their mol fractions from those of the oxides [7].

$\text{Si}_4\text{O}_8 = 0.25 \times [\text{SiO}_2 - 0.5(\text{FeO} + \text{MnO} + \text{MgO} + \text{NiO} + \text{CoO} + \text{CaO}) - \text{Na}_2\text{O} - \text{K}_2\text{O}]$
$\text{Ti}_4\text{O}_8 = 0.25 \times \text{TiO}_2$
$\text{Al}_{16/3}\text{O}_8 = 0.375 \times \text{Al}_2\text{O}_3$
$\text{Fe}_{16/3}\text{O}_8 = 0.375 \times \text{Fe}_2\text{O}_3$
$\text{Cr}_{16/3}\text{O}_8 = 0.375 \times \text{Cr}_2\text{O}_3$
$\text{Fe}_4\text{Si}_2\text{O}_8 = 0.25 \times \text{FeO}$
$\text{Mn}_4\text{Si}_2\text{O}_8 = 0.25 \times \text{MnO}$
$\text{Mg}_4\text{Si}_2\text{O}_8 = 0.25 \times \text{MgO}$
$\text{Ni}_4\text{Si}_2\text{O}_8 = 0.25 \times \text{CoO}$
$\text{Ca}_4\text{Si}_2\text{O}_8 = 0.25 \times \text{CaO}$
$\text{Na}_{16/3}\text{Si}_8/3\text{O}_8 = 0.375 \times \text{Na}_2\text{O}$
$\text{K}_{16/3}\text{Si}_8/3\text{O}_8 = 0.375 \times \text{K}_2\text{O}$
$\text{P}_{16/5}\text{O}_8 = 0.625 \times \text{P}_2\text{O}_5$
$\text{Sr}_8\text{O}_8 = 0.125 \times \text{SrO}$
$\text{H}_2\text{O} = 1 \times \text{H}_2\text{O}$

that only 55 out of these 120 parameters turn out to have significant values, so the others can thus be set equal to zero. Finally, as in Ghiorso's model, the excess Gibbs free energy of mixing does not depend on pressure; the volume, compressibility, and thermal expansion of the melt are obviously regarded as linear combinations of the values of its components. This “*isometric*” condition is however not compulsory for this class of models. Non-zero excess volumes are in fact necessary when describing, for instance, the P – T saturation hypersurface of $\text{H}_2\text{O} + \text{CO}_2$ fluids in natural magmas [8].

A remarkable feature for the model is its ability to account for the miscibility gaps observed in magmas. The topology of the Gibbs free energy of the mixing surface depicted in a multicomponent space may be rather complex. A saddle-shaped conformation may, for instance, describe spinodal decomposition as illustrated in Figure 3 by the partial derivative of the Gibbs free energy of mixing with respect to the mol fraction of the Si_4O_8 component:

$$\begin{aligned} \left(\frac{\partial G_{\text{mixing,melt}}}{\partial x_{\text{Si}_4\text{O}_8,\text{melt}}} \right)_{P,T,X_j} &= RT \ln a_{\text{Si}_4\text{O}_8,P,T,\text{melt}} \\ &= 4 \left(\mu_{\text{SiO}_2,P,T,\text{melt}} - \mu_{\text{SiO}_2,\text{melt}}^0 \right), \end{aligned} \quad (10)$$

where $a_{\text{Si}_4\text{O}_8,P,T,\text{melt}}$ is the thermodynamic activity of the Si_4O_8 component in the melt at the T , P of interest. In the SiO_2 -rich side of the diagram, spinodal decomposition at 1700 K is seen in Figure 3 as points b and d, implying fields of metastable homogeneity.

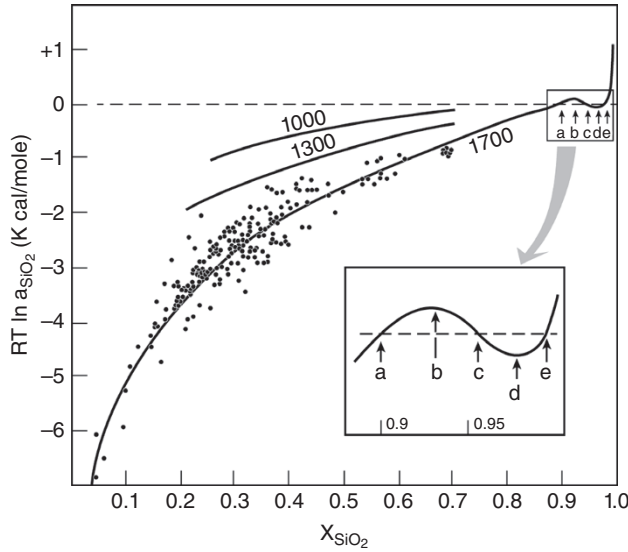


Figure 3 Ghiorso–Carmichael model [7]. Partial derivative of Gibbs free energy of mixing of melt with respect to Si_4O_8 component plotted against molar amount of silica in melt. Enlarged area: spinodal field of critical immiscibility (spinodal decomposition). Points = experimental observations.

From its first appearance on, the model has been continuously revised and “user-friendly” computer freeware codes have been developed. Based on the pioneering work of Ghiorso et al. recent releases (e.g. [9]) consider in detail the effect of pressure up to 3 GPa through calibration procedures based on an extended petrological database.

3.2 Fictive-Chemical Models: Mechanical Mixtures

The “*constitutional model*” [10] may be considered lying half way between the *fictive-chemical* and the *fictive-structural* classes. Although developed on a strictly chemical framework (i.e. that of *constitutional relations*), it implicitly contains structure-oriented concepts, inasmuch as the relative concentrations of components for a given bulk composition reflect the coexistence of short-range-order structural entities termed *chemical structure* [11].

The model is essentially based on the operative assumption that the heat capacity gaps between glass and crystal ($\Delta C_{p,g-c}$) and liquid and crystal ($\Delta C_{p,l-c}$) are nearly identical (ΔC_p) and constant in a wide T range. From the equalities,

$$S_{\text{vit}} + \int_{T_g}^T \frac{\Delta C_{p,g-c}}{T} dT = S_{\text{fus}} - \int_T^{T_{\text{fus}}} \frac{\Delta C_{p,l-c}}{T} dT, \quad (11)$$

$$H_{\text{vit}} + \int_{T_g}^T \Delta C_{p,g-c} dT = H_{\text{fus}} - \int_T^{T_{\text{fus}}} \Delta C_{p,l-c} dT, \quad (12)$$

where S_{vit} and S_{fus} are the entropy of vitrification at the glass transition T_g and the entropy of fusion, respectively, and H_{vit} and H_{fus} their enthalpic counterparts, one thus gets for $T \gg T_g$:

$$S_{\text{vit}} - \Delta C_p \ln \frac{T_g}{T} \approx S_{\text{fus}} - \Delta C_p \ln \frac{T_{\text{fus}}}{T}, \quad (13)$$

$$H_{\text{vit}} + \Delta C_p (T - T_g) \approx H_{\text{fus}} - \Delta C_p (T_{\text{fus}} - T). \quad (14)$$

With the above provisos, one calculates the thermodynamic quantities of the glass and the liquid by assuming the fictive components (k) to be those of *mechanical mixtures* (i.e. $\Delta H_{\text{mix}} = \Delta S_{\text{mix}} = 0$):¹

$$H_{\text{glass}}^0 = \sum_k n_k (H_k^0 + H_{\text{vit},k}); \quad S_{\text{glass}}^0 = \sum_k n_k (S_k^0 + S_{\text{vit},k}), \quad (15)$$

$$H_{1673,\text{liq}}^0 = \sum_k n_k H_{1673,\text{liq},k}^0; \quad S_{1673,\text{liq},k}^0 = \sum_k n_k S_{1673,\text{liq},k}^0, \quad (16)$$

$$C_{p,\text{liq}} = \sum_k n_k C_{p,\text{liq},k}, \quad (17)$$

$$H_{T,\text{liq}} = H_{1673,\text{liq}}^0 + C_{p,\text{liq}} (T - 1673), \quad (18)$$

$$S_{T,\text{liq}} = S_{1673,\text{liq}}^0 + C_{p,\text{liq}} \ln \left(\frac{T}{1673} \right). \quad (19)$$

In these Eqs. H_{glass}^0 and S_{glass}^0 are the standard enthalpy and entropy of the *rigid* glass at 298 K, 10^5 Pa, respectively, whereas $H_{1673,\text{liq}}^0$ and $S_{1673,\text{liq}}^0$ are the enthalpy and entropy of the melt at 1673.15 K, and $H_{T,\text{liq}}$, $S_{T,\text{liq}}$, and $C_{p,\text{liq}}$ are the enthalpy, entropy, and heat capacity of the melt at the high temperature T [10, 11]. One then obtains the molar amounts (n_k) and masses (m_k) of the fictive components from a normative deconvolution of the bulk glass or liquid composition by applying

$$\vec{n}_j = (\nu_{jk}) \cdot \vec{n}_k \Rightarrow \vec{n}_k = (A_{kj}) \cdot \vec{n}_j, \quad (20.1)$$

¹ The Gibbs energy of a mixture of oxide components i reads $G = \sum n_j \cdot G_j^\circ + \Delta G_{\text{mix}}$; G_j° = Gibbs energy of pure component i ; $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$. If the constitutional compounds k (in their crystalline, glassy, or liquid state, respectively) are chosen instead as frame of description, then $\Delta H_{\text{mix}} \rightarrow \text{nil}$ (coexistence = absence of interaction; ideal mixing) and $\Delta S_{\text{mix}} \rightarrow \text{nil}$ (N atoms accumulated in one entity k) brings Eq. (2) into the form $\Delta S_{\text{mix,id}} = -(R/N) \cdot \sum n_k \ln x_k$. Thus, written in the frame of k , the Gibbs energy assumes the form of a “*mechanical*” mixture $G = \sum n_k \cdot G_k^\circ$ (R. Conradt, pers. comm.).

$$\vec{m}_j = (\omega_{jk}) \cdot \vec{m}_k \Rightarrow \vec{m}_k = (B_{kj}) \cdot \vec{m}_j, \quad (20.2)$$

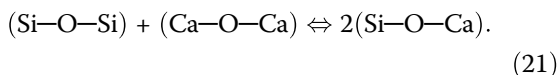
$$(A_{kj}) = (\nu_{jk})^{-1}, (B_{kj}) = (\omega_{jk})^{-1}. \quad (20.3)$$

where ν_{jk} is the matrix element indicating how many mols of oxide j are present in the fictive component k , ω_{jk} states how many kg of oxide j are contained in 1 kg of component, and A_{kj} and B_{kj} are the elements of the inverted matrices (ν_{jk}) and (ω_{jk}) , respectively. The thermodynamic data for the fictive components employed to represent the crystalline reference systems (c.r.s.) of industrial glasses and liquids are listed in Table 2. The chemical fragmentation of the system and the fact that a good part of the ideal and excess mixing terms is embodied in the standard state values of the fictive components ensures a sufficient precision for industrial purposes since the integral thermodynamic properties of glasses and melts are predicted to within uncertainties lower than 5% [11].

3.3 Fictive-Structural or Cellular Models

This third class of models aims at representing the reactive properties of the species actually present in chemically complex melts by relying on an *a priori* choice of structural features, such as the existence of particularly stable complexes in the mixture, or fictive-structural units.

Let us consider again CaO–SiO₂ binary melts. In the cellular model one assumes that they contain three structural units, with a bridging oxygen linked either to two silicon atoms (Si–O–Si), to one silicon and one calcium atoms (Si–O–Ca), or to two calcium atoms (Ca–O–Ca). These structural units mutually react with an energy change that can be assimilated to that of a quasi-chemical reaction of the type



An interaction energy change $2W_{ij}$ is associated to reaction (21). This energy is not sufficient to describe all interaction effects in the liquid phase, so an additional term E_{ij} is necessary to account for those between the (Si–O–Si) and (Si–O–Ca) moieties. The Gibbs free energy of the mixture is then given in terms of partition function Q :

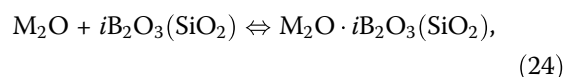
$$G_{\text{mixture}} = -RT \ln Q, \quad (22)$$

$$\ln Q = -\frac{E_0}{RT} + \ln g, \quad (23)$$

where E_0 is the energy of the (liquid) system in its stable configuration and g represents the configurational degeneracy of the system at E_0 . In the model assessment developed at IRSID [12], the interaction terms are expanded as a function of the molar fraction of the components to which the highest cationic charges are associated.

Although these adopted interaction terms do not depend on temperature, they dominate over the configurational effects. The resulting Gibbs free energy of mixing in the liquid phase is thus virtually unaffected by temperature. This peculiarity is common to other systems where silica is mixed with a strongly basic oxide (see Section 3.5) and has a deep intrinsic significance because the interaction is mostly dictated by the contrasting way in which the two oxides accept or donate oxygen ions in the sense of the Lux–Flood acid–base theory. For the CaO–SiO₂ system, good agreement is achieved by the cellular model in terms of six interaction parameters with, for instance, the experimentally observed activities of oxide components (Figure 4).

In the Shakhmatkin–Vedishcheva–Wright associated solution model developed for alkali-silicate and borate liquids and glasses [13–15], it is assumed that “*salt-like products*” or “*groupings*” [13] form between a generic metal oxide M_2O and the network formers within a restricted concentration range (0–50% M_2O) as described by the general reaction:



where i in the above equation is the stoichiometric amount of boron oxide (or silica) in the various groupings. It is assumed to correspond to what is observed in the crystalline compounds known to nucleate in the system of interest. The liquid (or glassy) mixture is assumed to be ideal, and the molar fractions of the various species are defined by [13]:

$$k_i = \frac{x_{M \cdot iB(\text{Si})}}{x_M \cdot x_B^i}, \quad (25)$$

$$x_M^* = \sum_i n_{M \cdot iB(\text{Si})} + n_M, \quad (26)$$

$$x_{B(\text{Si})}^* = \sum_i i \cdot n_{M \cdot iB(\text{Si})} + n_{B(\text{Si})}, \quad (27)$$

$$x_j = n_j / \left(\sum_i n_{M \cdot iB(\text{Si})} + n_M + n_{B(\text{Si})} \right). \quad (28)$$

where k_i is the equilibrium constant of reaction (24); $x_{M \cdot iB(\text{Si})}$, x_M , $x_{B(\text{Si})}$ are the mol fractions of the salt-like groupings and oxides, $n_{M \cdot iB(\text{Si})}$, n_M , $n_{B(\text{Si})}$ the molar amounts of the same species, and x_M^* , $x_{B(\text{Si})}^*$ the “*analytical*” composition of the investigated liquid or glass (i.e. $x_M^* + x_{B(\text{Si})}^* = 1$).

Assuming for simplicity that the equilibrium constants k_i in the liquid (or glass) are equal to those observed for the crystalline counterparts (and, as such, readily obtainable from the tabulated values of the Gibbs free energy of formation from the elements of the simple oxides and

Table 2 Thermodynamic data of fictive components k employed to represent the crystalline reference systems (c.r.s.) of industrial glasses and liquids [10, 11]⁶; enthalpies H in kJ/mol, entropies S , and heat capacities C_p in J/(mol·K); superscripts, ° = standard state at 298.15 K, 1 bar; subscripts, vit = vitrification; liq = liquid state; 1673 = 1673.15 K.

k	$-H^\circ$	S°	H_{vit}	S_{vit}	$-H_{1673,liq}$	$S_{1673,liq}$	$C_{p,liq}$
P ₂ O ₅ ·3 CaO	4117.1	236.0	135.1	51.5	3417.1	898.7	324.3
P ₂ O ₅	1504.9	114.4	18.2	9.5	1151.5	586.6	181.6
Fe ₂ O ₃	823.4	87.4	45.2	17.2	550.2	370.3	142.3
FeO·Fe ₂ O ₃	1108.8	151.0	82.8	31.4	677.8	579.9	213.4
FeO·SiO ₂	1196.2	92.8	36.7	13.8	962.3	342.7	139.7
2 FeO·SiO ₂	1471.1	145.2	55.2	20.5	1118.8	512.1	240.6
MnO·SiO ₂	1320.9	102.5	40.2	15.1	1085.3	345.2	151.5
2 ZnO·SiO ₂	1643.1	131.4	82.4	31.4	1261.1	494.5	174.5
ZrO ₂ ·SiO ₂	2034.7	84.5	86.6	32.6	1686.2	381.2	149.4
CaO·TiO ₂	1660.6	93.7	67.4	25.5	1365.7	360.2	124.7
BaO·Al ₂ O ₃ ·2 SiO ₂	4222.1	236.8	130.5	95.4	3454.3	1198.3	473.2
BaO·2 SiO ₂	2553.1	154.0	81.6	26.8	2171.1	533.5	241.4
BaO·SiO ₂	1618.0	104.6	56.5	41.0	1349.8	361.1	146.4
Li ₂ O·Al ₂ O ₃ ·4 SiO ₂	6036.7	308.8	184.1	12.1	5235.4	1173.2	498.7
Li ₂ O·SiO ₂	1648.5	79.9	16.7	6.31	416.7	339.7	167.4
K ₂ O·Al ₂ O ₃ ·6 SiO ₂	7914.0	439.3	106.3	29.3	6924.9	1559.4	765.7
K ₂ O·Al ₂ O ₃ ·2 SiO ₂	4217.1	266.1	80.4	22.1	3903.7	666.5	517.6
K ₂ O·4 SiO ₂	4315.8	265.7	26.4	21.3	3697.8	983.7	410.0
K ₂ O·2 SiO ₂	2508.7	190.6	12.6	23.9	2153.1	595.4	275.3
Na ₂ O·Al ₂ O ₃ ·6 SiO ₂	7841.2	420.1	125.0	28.4	6870.1	1512.5	648.1
Na ₂ O·Al ₂ O ₃ ·2 SiO ₂	4163.5	248.5	92.0	27.9	3614.1	856.9	423.8
B ₂ O ₃	1273.5	54.0	18.2	11.3	1088.7	271.1	129.7
Na ₂ O·B ₂ O ₃ ·4 SiO ₂	5710.9	270.0	42.7	21.1	4988.0	1090.2	637.6
Na ₂ O·4 B ₂ O ₃	5902.8	276.1	58.3	40.1	4986.7	1275.5	704.2
Na ₂ O·2 B ₂ O ₃	3284.9	189.5	48.8	26.6	2735.9	780.3	444.8
Na ₂ O·B ₂ O ₃	1958.1	147.1	43.6	19.5	1585.7	538.7	292.9
2 MgO·2 Al ₂ O ₃ ·5 SiO ₂	9113.2	407.1	135.8	41.4	7994.8	1606.2	1031.8
MgO·SiO ₂	1548.5	67.8	46.6	13.6	1318.0	296.2	146.4
2 MgO·SiO ₂	2176.9	95.4	61.4	11.0	1876.1	402.9	205.0
CaO·MgO·2 SiO ₂	3202.4	143.1	92.3	25.7	2733.4	621.7	355.6
2 CaO·MgO·2 SiO ₂	3876.9	209.2	106.7	32.0	3319.2	775.3	426.8
CaO·Al ₂ O ₃ ·2 SiO ₂	4223.7	202.5	103.0	37.7	3628.8	791.2	380.7
2 CaO·Al ₂ O ₃ ·SiO ₂	3989.4	198.3	129.9	49.4	3374.0	787.8	299.2
CaO·SiO ₂	1635.1	83.1	49.8	18.8	1382.0	329.7	146.4
2 CaO·SiO ₂	2328.4	120.5	101.3	38.5	1868.2	509.2	174.5
Na ₂ O·2 SiO ₂	2473.6	164.4	29.3	13.2	2102.5	588.7	261.1
Na ₂ O·SiO ₂	1563.1	113.8	37.7	9.81	288.3	415.1	179.1
Na ₂ O·3 CaO·6 SiO ₂	8363.8	461.9	77.3	20.5	7372.6	1555.6	786.6
Na ₂ O·2 CaO·3 SiO ₂	4883.6	277.8	57.7	13.4	4240.9	990.4	470.3
2 Na ₂ O·CaO·3 SiO ₂	4763.0	309.6	87.0	22.6	4029.6	1107.9	501.2
SiO ₂	908.3	43.5	6.9	4.0	809.6	157.3	86.2

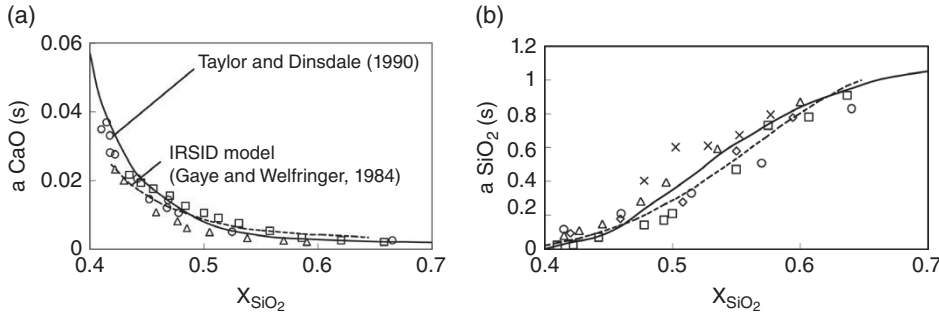


Figure 4 Component activities in CaO-SiO₂ melts at 1823 K and 1 bar: predictions from the cellular model developed at IRSID (dashed lines) [12] and from the modified version of Taylor and Dinsdale (solid lines) [16] are compared with various experimental results at similar temperatures (open symbols).

their salts), the Gibbs free energy of formation of the liquid (or glass) of interest ΔG_f is obtained as

$$\Delta G_f = \sum_i n_i \Delta G_i^0 + RT \sum_j n_j \ln x_j \quad (29)$$

where the i summation is taken only over the salt-like groupings while that in j includes the unreacted oxides.

The application to alkali silicate and borate glasses reveals a remarkable model capability to reproduce the observed NMR experimental speciation [13–15] and other relevant structural data available in literature.

3.4 Quasi-Chemical Models

With quasi-chemical approaches, the energy involved in discrete interactions among quasi-species in solution is investigated in detail. Contrary to the previous ones, these models assign a precise structural meaning to these interactions.

Specifically [17], they assume that in a binary system with components 1 and 2, the 1 and 2 *particles* mix substitutionally in a quasi-lattice obeying a short-range ordering dictated by the equilibrium

$$[1-1] + [2-2] \rightleftharpoons 2[1-2], \quad (30)$$

with some analogy with Eq. (21). The molar enthalpy change associated with equilibrium (30) is expressed in terms of pairwise bond energies ε_{ij} :

$$\omega = \frac{Nz}{2} (2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22}), \quad (31)$$

where N and z denote the number and coordination of the complex, respectively.

The nonconfigurational part of the molar entropy is also given in terms of bond contributions η_{ij} (nonconfigurational entropy of the ij pair bond):

$$\eta = \frac{Nz}{2} (2\eta_{12} - \eta_{11} - \eta_{22}). \quad (32)$$

We will denote by x_{ij} the mol fraction of the ij particle with respect to the total of the particles formed in the

system. Since each atom i is bonded to z_i neighbors, it follows from mass balance that

$$\frac{x_{12}}{2} = (x_1 - x_{11}) = (x_2 - x_{22}). \quad (33)$$

The enthalpy of mixing then becomes

$$H_{\text{mixing}} = \frac{x_{12}}{2} \omega. \quad (34)$$

The nonconfigurational (excess) entropy of mixing is

$$S_{\text{mixing,non-conf}} = \frac{x_{12}}{2} \eta, \quad (35)$$

and the configurational (ideal + excess) entropy of mixing is

$$S_{\text{mixing,conf}} = -R(x_1 \ln x_1 + x_2 \ln x_2) - \frac{Rz}{2} \left(x_{11} \ln \frac{x_{11}}{x_1^2} + x_{22} \ln \frac{x_{22}}{x_2^2} + x_{12} \ln \frac{x_{12}}{2x_1x_2} \right). \quad (36)$$

The equilibrium concentrations of the various pairs are determined by the minimum of the Gibbs free energy:

$$\frac{\partial G_{\text{mixing}}}{\partial x_{12}} = \frac{\partial (H_{\text{mixing}} - TS_{\text{mixing}})}{\partial x_{12}} = 0. \quad (37)$$

Through appropriate expansions in terms of Eqs. (34)–(36), one then obtains

$$\frac{x_{12}^2}{x_{11}x_{22}} = 4 \exp \left[\frac{-2(\omega - \eta T)}{zRT} \right]. \quad (38)$$

The name “*quasi-chemical*” assigned to the model stems from the fact that the right-hand term in Eq. (38) reduces to a constant for constant values of ω and η . This expression thus resembles a chemical reaction among ideal [1-1], [2-2] reactants and [1-2] product.

From Eq. (38) one gets [18]

$$\frac{x_{12}}{2} = \frac{2x_1x_2}{1 + \xi}, \quad (39)$$

where

$$\xi = \left\{ 1 + 4x_1x_2 \left[\exp \left(\frac{2(\omega - \eta T)}{zRT} \right) - 1 \right] \right\}^{1/2}. \quad (40)$$

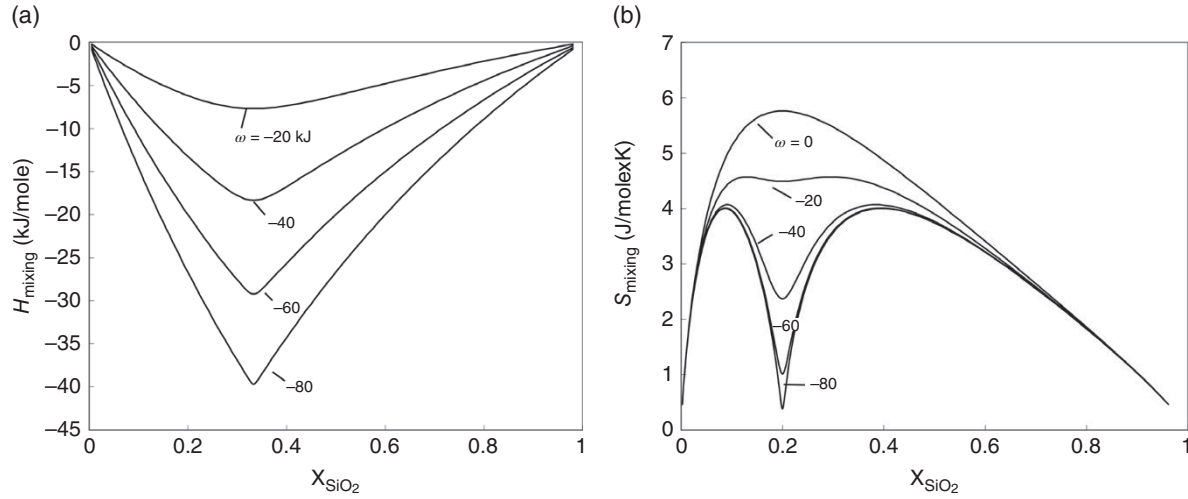


Figure 5 Integral mixing properties for different values of the interaction parameter ω in the quasi-chemical model of binary SiO_2 -MO join: (a) enthalpy; (b) entropy.

The model is resolved first in terms of equilibrium distribution of particles with Eqs. (32) and (39) and (40) and then in terms of enthalpy and entropy with Eqs. (33) and (34) and (35), respectively.

The computed enthalpy and entropy terms have a typical V-shaped and M-shaped conformation; the more pronounced, the more negative the value assigned to ω . The quasi-chemical enthalpies and entropies of mixing computed with $z = 2$, $\eta = 0$ and various values of ω are shown for comparison in Figure 5 for a $\text{MO-Si}_{0.5}\text{O}$ system. When ω and η are set equal to zero, the mixture is obviously ideal, whereas the mixture is strictly regular when $\eta = 0$ and $x_{12} = 2 x_1 x_2$. In all cases the properties of the mixture are depicted however as asymmetric in the compositional space of interest.

The asymmetry about the intermediate composition has long been regarded as a severe limitation of the quasi-chemical model when applied to silicate melts (slags included), because it yields consistently maximum ordering about the composition $x_{\text{MO}} = 2/3$ in the MO-SiO_2 chemical space. To render symmetric the maximum ordering condition embodied by this model – i.e. to make it consistent with Eq. (2) – the true molar fractions x_1 , x_2 may be substituted with “equivalent fractions” y_1 , y_2 such that [18]

$$y_1 = \frac{b_1 x_1}{b_1 x_1 + b_2 x_2}; \quad (41.1)$$

$$y_2 = \frac{b_2 x_2}{b_1 x_1 + b_2 x_2}. \quad (41.2)$$

The coefficients b_1 and b_2 are chosen in such a way as to ensure $b_1/(b_1 + b_2) = 1/3$ and $b_2/(b_1 + b_2) = 2/3$. One readily sees that when $x_1 = 2/3$ and $x_2 = 1/3$, we have $y_1 = y_2 = 0.5$.

To assign more computational flexibility to the model, the ω and η parameters are finally expanded as polynomial functions of the equivalent fractions y_1 , y_2 , viz.

$$\omega = \omega_0 + \omega_1 y_2 + \omega_2 y_2^2 + \dots \omega_n y_2^n, \quad (42.1)$$

$$\eta = \eta_0 + \eta_1 y_2 + \eta_2 y_2^2 + \dots \eta_n y_2^n. \quad (42.2)$$

Extension to a ternary system, $\text{AO}_x - \text{BO}_y - \text{CO}_z$ (A–B–C hereafter) system is not straightforward because it involves the adoption of ternary interaction parameters, which may be obtained only by inverse modeling operating on the topology of the liquidus hypersurface. The Pelton–Blander modified quasi-chemical model is at the core of the FactSage commercial package (www.factsage.com), widely used in metallurgy and in the glass industry. Its precision in reproducing the experiments is remarkable thanks to the flexibility of the computational approach. As an example, the liquidus projection (univariant cotectics and invariant points) of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system (CAS) is shown in Figure 6 as resolved by the FACT program. The phase relations in a binary system (i.e. a *Simplex* of degree 1) are readily represented graphically to indicate the equilibrium temperature of a given composition along the liquidus curve (Figure 2). For a ternary system (i.e. a *Simplex* of degree 2), however, the temperature information is necessarily lost in a 2-D plot so that isotherms are usually superimposed on the univariant liquidus hypersurfaces to depict their 3-D nature.

3.5 Polymeric Approach

In polymeric models, one postulates that, for each composition at given values of P and T , the melt is characterized by an equilibrium distribution of ionic species of

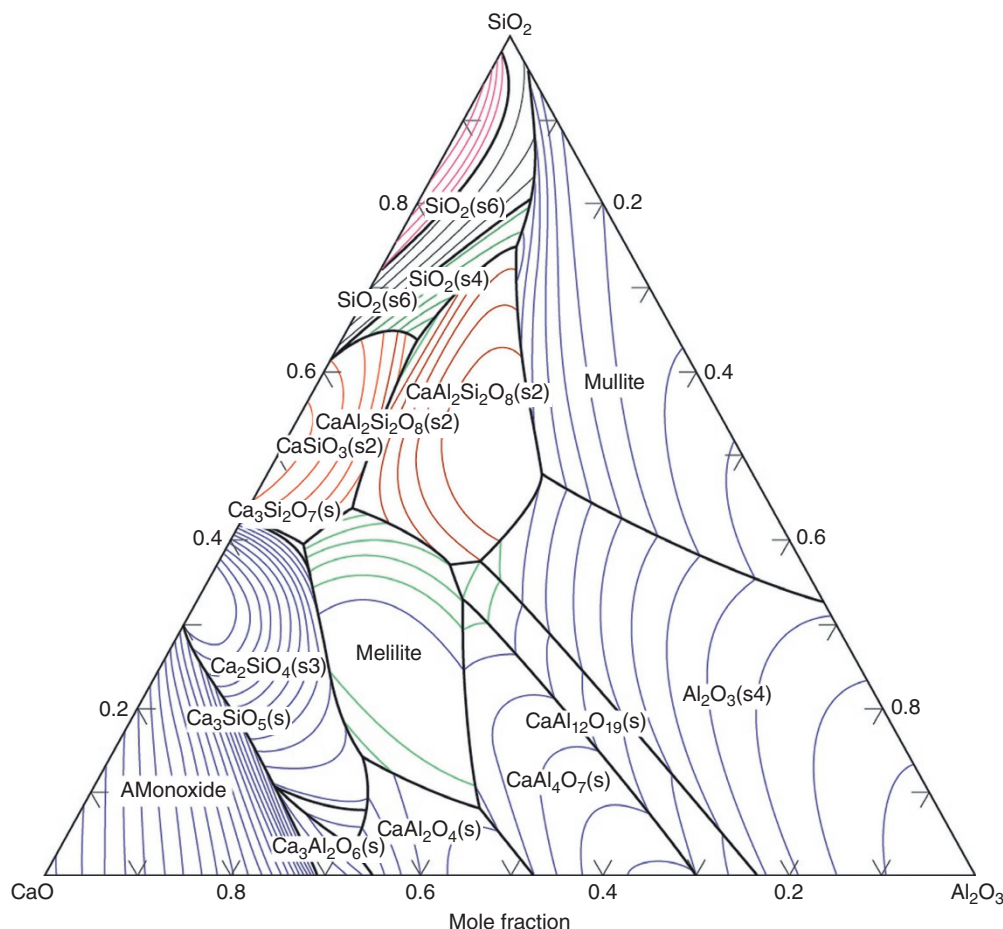
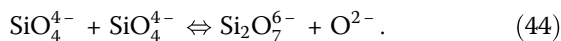


Figure 6 Solid–liquid equilibria calculated for the CaO–Al₂O₃–SiO₂ system with the FACT commercial package (<http://www.factsage.com>).

oxygen, metal cations, and ionic polymers of monomeric units SiO_4^{4-} . The charge balance of a polymerization reaction involving SiO_4^{4-} monomers may be formally described by a homogeneous reaction involving three forms of oxygen [19]: singly bonded O^- , doubly bonded (or *bridging oxygen*) O^0 , and free oxygen ions O^{2-} :



In fact, Eq. (43) is similar to a reaction between SiO_4^{4-} monomers:



A fundamental principle of polymer chemistry is that the reactivity is independent of the effective length of the polymer chains (cf. Chapter 8.8). It then follows [20] that this principle applies to the equilibrium constant of Eq. (43), which is

$$K_{43} = \frac{(\text{O}^0)(\text{O}^{2-})}{(\text{O}^-)^2}, \quad (45)$$

where the terms in parentheses represent the number of moles per unit mole of melt.

In a binary system MO–SiO₂, in which MO is the oxide of a completely dissociated basic cation, the total number of bonds per mole of melt is given by [21]

$$2(\text{O}^0) + (\text{O}^-) = 4N_{\text{SiO}_2}, \quad (46)$$

where N_{SiO_2} is the mol fraction of SiO₂. The number of bridging oxygens is thus

$$(\text{O}^0) = \frac{4N_{\text{SiO}_2} - (\text{O}^-)}{2}. \quad (47)$$

Mass balance gives the number of moles of free oxygen per mole of melt:

$$(\text{O}^{2-}) = (1 - N_{\text{SiO}_2}) - \frac{(\text{O}^-)}{2}, \quad (48)$$

where $(1 - N_{\text{SiO}_2})$ are the number of moles of the basic oxide. Then, Eqs. (46)–(48) yield

$$K_{43} = \frac{[4N_{\text{SiO}_2} - (\text{O}^-)][2 - 2N_{\text{SiO}_2} - (\text{O}^-)]}{4(\text{O}^-)^2}. \quad (49)$$

Finally (O^-) is given by the quadratic equation

$$(O^-)^2(4K_{43} - 1) + (O^-)(2 + 2N_{SiO_2}) + 8N_{SiO_2}(N_{SiO_2} - 1) = 0, \quad (50)$$

which may be solved for discrete values of K_{43} and N_{SiO_2} .

The symmetry problems encountered with the quasi-chemical model are *a priori* discarded because the ideal mixing terms are implicitly part of the bulk Gibbs free energy of mixing contribution, weighted in terms of $(O^-)/2$ contacts:

$$G_{\text{mixing}} = \frac{(O^-)}{2} RT \ln K_{43}. \quad (51)$$

The chemical interactions within the anion matrix of a n -component system are completely fixed by the interaction properties observed along the $n - 1$ limiting binaries [1, 22]. Denoting by $K_{P,A-F}$, $K_{P,B-F}$ the polymerization constants valid along the limiting A-F and B-F binaries, the polymerization constant of the extended Toop-Samis model turns out to be

$$\ln K_P = N'_{A^{v+}} + \ln K_{P,A-F} + N'_{B^{v+}} + \ln K_{P,B-F} + \dots \quad (52)$$

For a compositionally complex melt, the above equation states that network-modifier cations A, B of charge ν_A^+ , ν_B^+ interact with free oxygen O^{2-} (and hence with

the polymeric units built up by the network former F) according to a simple proportionality described in terms of $N'_{A^{v+}}$, $N'_{B^{v+}}$ “electrically equivalent fractions” [22, 23]:

$$N'_{A^{v+}} = \frac{\nu_A^+ n_A}{\nu_A^+ n_A + \nu_B^+ n_B + \dots} \quad (53)$$

In light of this fact, it is possible to depict the thermodynamic properties of an n -component system through Toop’s asymmetric deconvolution (i.e. with the assumption that the cation matrix is not appreciably affected by anions while the anion matrix is affected by cations). As an example, the phase diagram of the CAS system calculated with the hybrid polymeric approach [1, 2] is shown in Figure 7. The 3-D representation emphasizes the role of temperature in conforming the liquidus. The porcelain rendering adopted to stress the importance of this system in ceramurgy should not be overlooked. The complex liquidus hypersurface was indeed obtained through convex-hull techniques [24] applied to a simplicial mesh (i.e. a mesh made up of the simplest polytypes) of 2×10^6 energy points for each temperature investigated.

4 First-Principles Calculations

Describing the application of first-principles methods to phase-equilibrium calculations is clearly beyond the

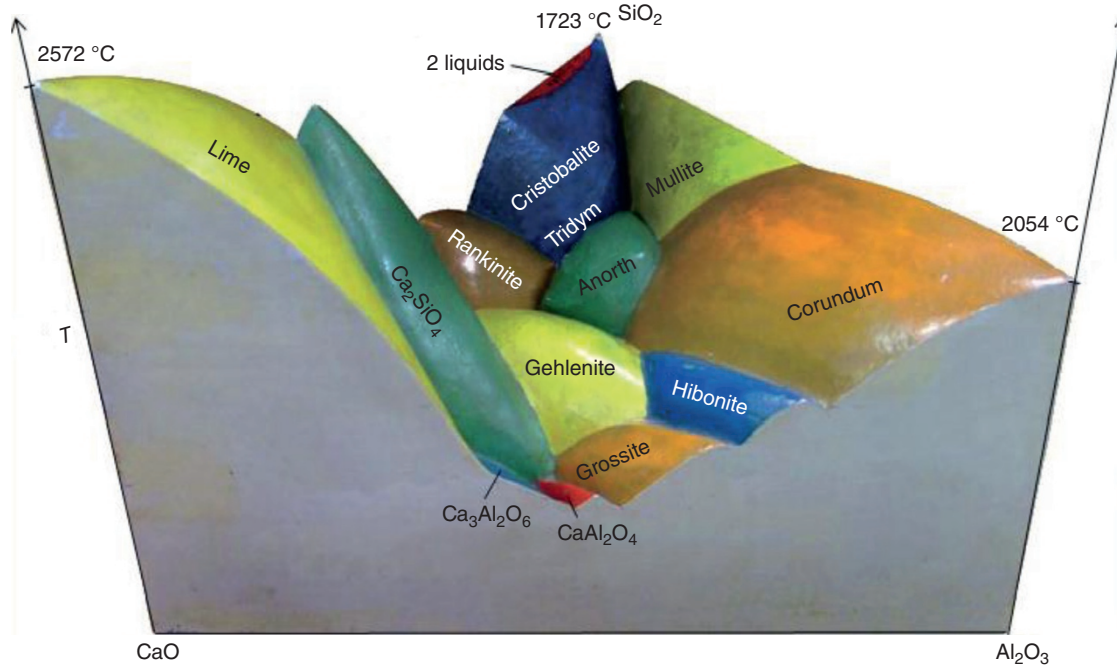


Figure 7 Solid-liquid equilibria calculated for the CaO-Al₂O₃-SiO₂ system with the hybrid polymeric approach [2]. The liquidus hypersurface was resolved through convex-hull techniques on a simplicial mesh of $100 \times 100 \times 100$ energy points for each temperature at 1 K scale discretization in the range 1000–3000 K. The surface was then smoothed, and a porcelain-like rendering of the diagram was selected to emphasize the importance of this system in ceramurgy.

scope of this chapter. Referring to Chapter 2.10 for a brief summary of their fundamental features, we will simply illustrate how results currently obtained indicate that the empirical coefficients of thermodynamic models will be soon substituted with energy terms arising from quantum-mechanical assessments. Of special interest in this respect is the recent finding [25] that polarizable ionic liquids such as silicate melts may be treated within the framework of the polarized continuum model (PCM) of Tomasi and coworkers [26].

The solvent parameters of silicate liquids treated as polarized continua in the framework of the Pierotti–Reiss scaled particle theory, coupled with the PCM, have in fact already been resolved on the basis of the plethora of high-temperature solubility experiments on inert gases [25]. In particular, silicate melts behave as ionic liquids of medium polarizability with dielectric properties intermediate between water and benzene whose effective solvent electrostatic radii (r_e) may be readily obtained with a scalar operation based on the collisional radius of Eyring (r_{coll}) [27]:

$$r_e = 1.138 \times r_{\text{coll}} - 0.3836 \text{ (Å)}. \quad (54)$$

A first application to the H_2O – SiO_2 system [28] has revealed that the solubility of molecular water in molten silica is indeed more complex than thought, being favored at low $X_{\text{H}_2\text{O}}$ content in the liquid by hydrogen bonding between molecular water (OH_2) and the hydroxyl terminations (OH°) replacing singly bonded oxygens (O°) on the terminations of polymer chains. The results of detailed calculations are listed in Table 3 carried out

for discrete compositions along the wet solidus of the H_2O – SiO_2 system and for the limiting compositions (i.e. pure H_2O at $T = 25^\circ\text{C}$, $P = 1$ bar and pure silica liquid at $T = 1723^\circ\text{C}$, $P = 1$ bar). The dramatic increase of Henry's law constant with temperature (last two rows) is due to the essentially entropic nature of the cavitation energy. Also note how intense are the (electrostatic + dispersive + repulsive) solute–solvent interactions (computed at the B3LYP/6-31 + $G(d, p)$ theory level within the framework of PCM and here collected in a comprehensive interaction term).

5 Perspectives

The variety of conceptual models hitherto proposed by metallurgists, ceramists, and geochemists may seem disconcerting because most of them are valid only over a limited part of the n -component systems of interest to their fields. In addition, the wealth of experimental information available that range from petrological phase diagrams and gas-phase equilibration studies to electrochemical galvanic-cell and calorimetric measurement and structural investigations, which should be taken into account, represent a formidable challenge and could lead to a pessimistic view about the possibility of a unifying approach to melt energetics. The giant steps achieved by computer science in terms of calculation speed and memory storage capabilities of parallel devices, however, now render feasible first-principles investigation of medium- and long-range disordered substances.

Table 3 Scaling particle theory energy terms [28]. The cavitation enthalpy at P of interest and T of reference ($H_{\text{cav},P,\text{Tr}}$), the interaction energy ($H_{\text{int},P,\text{Tr}}$ assumed as purely enthalpic), and the cavitation Gibbs free energies ($G_{\text{cav},P,\text{Tr}}$; $G_{\text{cav},P,T}$) are in kJ/mol. The cavitation entropy ($S_{\text{cav},P,\text{Tr}}$) is in J/(mol K). Volume terms are in cc/mol. $K_{P,\text{Tr}}$ and $K_{P,T}$ are the Henry's Law constants for H_2O in pure silica liquid at T_r , P_r of reference ($T_r = 298.15$ K; $P_r = 10^5$ Pa) and T , P of interest, respectively.

$X_{\text{H}_2\text{O}}$	1	0.335	0.244	0.184	0.133	0.098	0.0583	0
P (bar)	1	10 000	7500	5000	2500	1250	500	1
f (bar)	1	19 610	11 380	5940	2520	1180	577	1
T ($^\circ\text{C}$)	25	1080	1065	1070	1100	1170	1300	1723
$H_{\text{cav},P,\text{Tr}}$	2.9	13.0	9.7	6.6	3.4	1.8	0.8	1.3
$S_{\text{cav},P,\text{Tr}}$	–52.6	–57.1	–57.8	–58.3	–58.7	–59.0	–59.3	–59.7
$V_{\text{cav},P,\text{Tr}}$	12.2	13.7	13.9	14.0	14.1	14.2	14.3	14.4
$G_{\text{cav},P,\text{Tr}}$	18.6	30.0	27.0	23.9	20.9	19.4	18.5	17.8
$G_{\text{cav},P,T}$	18.6	94.1	89.8	86.9	85.5	88.1	94.8	119.2
$H_{\text{int},P,\text{Tr}}$	–45.1	–56.1	–52.8	–52.6	–55.3	–60.5	–65.1	–40.6
$V_{\text{int},P,\text{Tr}}$	–0.250	–2.462	–2.593	–2.764	–3.069	–3.480	–3.898	–2.565
$V_{\text{solute},P,\text{Tr}}$	11.934	11.300	11.386	11.361	11.179	10.852	10.532	12.007
$\ln K_{P,\text{Tr}}$	–3.45	–3.53	–3.49	–4.64	–6.98	–9.71	–11.98	–2.35
$\ln K_{P,T}$	–3.45	11.81	11.73	11.46	11.04	10.73	10.77	13.47

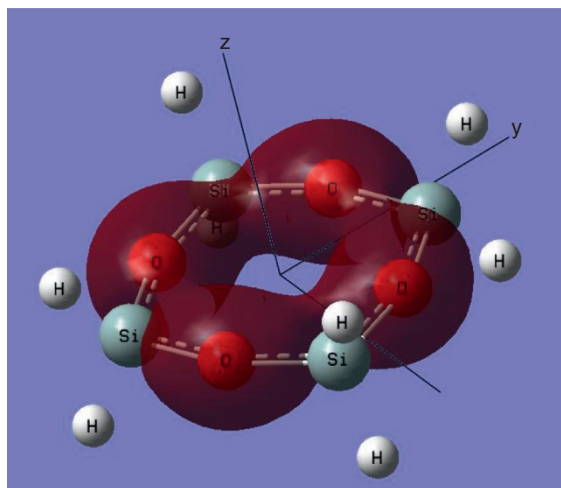


Figure 8 The σ -bonding orbitals of the $[\text{Si}_4(\text{OH}_2)_4]$ ring resolved at the B3LYP/TZVP theory level. The isodensity limit is $0.03 \text{ e}/\text{\AA}^3$ for both structures, the eigenvalue of the four-membered ring is -1.019 hartree, and that of the six-membered ring is -1.016 hartree. The electron clouds occupy essentially the xy plane in a standard arrangement [29].

That first-principles calculations reproduce experimental observations in heterogeneous P, T, x ranges makes us optimistic about the impact that full quantum chemistry applications will soon have for this class of substances. The road toward this goal is nevertheless still long and complex as new discoveries might render the target more distant than previously thought. We may quote in this respect the recent findings about the existence of the Pauling double bond between oxygen donor centers in silicate and silico-aluminate rings in the liquid [29]. Approaching cationic centers to the oxygen donors of the ring (z -axis in Figure 8), one observes a stabilizing effect in terms of orbital energy of the low-lying σ -bonding and antibonding molecular orbitals (MOs). Moreover, a detailed electron localization/delocalization analysis reveal an enhanced electron delocalization among O atoms, which is manifested in the Pauling's double bond nature of the bent σ -bonding MO between nonadjacent oxygen centers. This complex phenomenon acts in the direction opposite to what is commonly assumed with the statement that a basic oxide favors melt depolymerization by freeing oxygen donors. Even though new concepts may add further complexities, we confidently expect that further theoretical work will give a sounder basis to thermodynamic models and make them applicable to wider composition, temperature, and pressure ranges. In view of their complexity and of the very long computing times required for large systems, however, it is unlikely that such first-principles calculations will make, in a near future, the models described in this chapter obsolete for routinely predictions on phase equilibria.

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5.4

Nucleation, Growth, and Crystallization in Inorganic Glasses

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1 Introduction

When any liquid is cooled below its equilibrium melting or *liquidus* temperature, one or several crystalline phases may form. This process takes place in two steps: the formation of clusters and their subsequent evolution to macroscopic crystals. The first step is denoted *nucleation*, and the second is *crystal growth*. The effect of simultaneous crystal nucleation and growth is denominated *crystallization*. Crystallization counteracts vitrification, the freezing of a melt into a glass. Upon heating, the same phenomenon results in glass devitrification.

Eight decades ago, G.W. Morey [1] stated that “Devitrification is the chief factor which limits the composition range of practical glasses, it is an ever-present danger in all glass manufacture and working, and takes place promptly with any error in composition or technique.” The prevention of crystal nucleation and growth upon cooling of any liquid – or upon heating of gels – gives rise to a glass. On the other hand, the global acceleration of technological breakthroughs, marked by high-tech industrial processes and devices, requires materials with unusual microstructures and enhanced or novel properties, such as transparency, bioactivity, ionic conductivity, or machinability, sometimes combined with excellent dielectric, magnetic, chemical, mechanical, or thermal shock resistance.

To meet this demand, significant efforts have focused on the synthesis of new glasses and glass ceramics. In both cases, crystallization control plays such a decisive role that

reliable models of crystallization processes are needed. Hence, knowledge about the possible pathways of crystallization allows one to formulate kinetic criteria to answer the questions: “Under what conditions can a liquid supercool and transform into a glass, and under what conditions is substantial crystallization expected to occur on the cooling path?” In attempts to produce new glasses, crystal nucleation and growth must be avoided. Conversely, controlled crystallization can be used to synthesize fully crystallized materials or semicrystalline glass ceramics (Chapter 7.11). Several monographs provide detailed information on these materials (e.g. [2, 3]).

However, these technological aspects represent only one side of the widespread scientific interest in the kinetics of nucleation and crystallization in glasses. In addition to their practical relevance, glass-forming liquids serve as remarkable experimental models of metastable, highly viscous systems, in which crystallization and liquid–liquid phase separation processes can be quickly initiated, accelerated, or delayed. These processes can thus be studied conveniently under very different conditions on a laboratory timescale. Such analyses may even include the dependence of the kinetics of phase formation on the thermal history of the sample. For this reason, glass-forming liquids have served as *guinea pigs* for testing crystal nucleation and growth theories, providing a deeper insight into different phase formation processes. And lastly, crystallization produces impressive, uniquely beautiful (and frequently hidden) nano- and microstructures, as demonstrated by E.D. Zanotto [4], which serves as an additional motivation to join and pursue research in this endless, albeit highly gratifying quest to unveil the deeply hidden intricacies of glass crystallization and the resulting properties of glass ceramics.

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To prevent or induce controlled crystal nucleation and growth in a glass requires some theoretical understanding of these complex phenomena. This chapter, therefore, outlines the basic fundamental aspects of the theory of crystallization of supercooled inorganic glass-forming liquids. Section 2 begins with a description of crystal nucleation kinetics, followed in Section 3 by an overview of some basic modes of crystal growth. Section 4 describes overall crystallization kinetics, i.e. the evolution of the volume fraction of crystalline phases as a function of time by nucleation and growth. In addition to some well-established results, we also briefly discuss some open problems and possible approaches to their resolution. A summary of relevant results and perspectives for future developments (Section 5) completes this chapter.

2 Crystal Nucleation and Classical Nucleation Theory

The physical nature of nucleation phenomena in general and crystal nucleation in supercooled liquids in particular was first established and described by J.W. Gibbs [5]. His basic idea can be illustrated by the following approximation for the change of Gibbs free energy, ΔG , during crystal cluster formation:

$$\Delta G = -n \Delta\mu + \sigma A, \Delta\mu = \mu_l - \mu_{cr}, A = 4\pi R^2, n = \frac{4\pi}{3} c_\alpha R^3. \quad (1)$$

In formulating Eq. (1), it is assumed that spherical crystalline nuclei form in an initially homogeneous liquid. These nuclei are described by their radius, R ; surface area, A ; and the number, n , of particles (atoms, molecules, or more generally the basic structural units of the crystalline phase) they contain. In Eq. (1), $\Delta\mu$ is the difference of the chemical potentials per particle in the liquid (μ_l) and the crystal (μ_{cr}), σ is the specific interfacial energy, and c_α is the particle number density in the crystal cluster. From the specification of the parameters, it is evident that Eq. (1) is valid only for the simplest case of crystallization when liquid and crystal consist of the same structural units. This kind of crystallization is denoted as *congruent*. Also, it is assumed here that the state of the crystal clusters is independent of their sizes. Qualitatively, the situation does not change in general cases of *incongruent* crystallization, when the crystal and liquid phases have different compositions.

According to thermodynamic evolution criteria, at constant pressure, P , and temperature, T , spontaneous macroscopic processes are tied to a decrease in the Gibbs free energy, G , of the system. For this reason, if $\mu_l < \mu_{cr}$ and $\Delta\mu = (\mu_l - \mu_{cr}) < 0$, ΔG in Eq. (1) is a monotonically increasing

function of cluster size for any possible values of R , so that crystal clusters of any size will disappear over time. The function $\Delta G = \Delta G(R)$ takes on the shape shown in Figure 1a only if the thermodynamic driving force for crystallization, $\Delta\mu$, is positive ($\mu_{cr} < \mu_l$). In this case, cluster formation and growth are accompanied by a decrease in the Gibbs free energy if the surface term in the expression for ΔG is neglected. However, this tendency for decreasing Gibbs free energy is counteracted by the surface term, i.e. the surface contribution to Gibbs free energy initially leads to an increase in ΔG with increasing crystal size. Small crystal clusters formed in the system disappear, and only clusters larger than a critical size, R_c , can grow to macroscopic dimensions. As demonstrated in Figure 1a, the critical cluster size is defined by the maximum of $\Delta G(R)$. Systems showing such behavior are denoted as metastable. Metastable states are stable with respect to small fluctuations (generating clusters with sizes $R < R_c$) but unstable with respect to larger fluctuations (leading to clusters with sizes $R > R_c$). Thus, viable (supercritical) crystal clusters capable of deterministic growth must exceed a critical size. It is this criticality that determines the crucial impact of these embryos of the newly evolving phase on the nucleation processes.

Taking the chemical potential difference and the specific interfacial energy as constants (i.e. employing the so-called “capillarity” approximation), one can derive the critical cluster size and the value of ΔG_c at the critical size from the extremum condition $d(\Delta G)/dR = 0$. These parameters are given by

$$R_c = \frac{2\sigma}{c_\alpha \Delta\mu}, \Delta G_c = \frac{1}{3} \sigma A_c = \frac{16\pi}{3} \frac{\sigma^3}{(c_\alpha \Delta\mu)^2}, A_c = 4\pi R_c^2. \quad (2)$$

These relations remain valid if more accurate expressions for $\Delta\mu$ are employed and the curvature dependence of the interfacial energy is accounted for. The concepts discussed above are illustrated in Figure 1a within the framework of the classical model of nucleation, whereby the change in the Gibbs free energy of cluster formation reaches a maximum $\Delta G = \Delta G_c$ for the critical cluster size, $R = R_c$. In this model, the clusters grow or decay while preserving their properties, so size is the only parameter specifying the state of the cluster.

A more realistic picture of cluster formation is presented in Figure 1b, where not only the size but also the composition (described by the number of particles, n_i , of two components) of the cluster may change. In this case, the critical cluster corresponds to a saddle point of the Gibbs free energy surface. The evolution to the new phase via the saddle is shown by the dark (red in the colored version) curve. In Figure 1c, we show an alternative

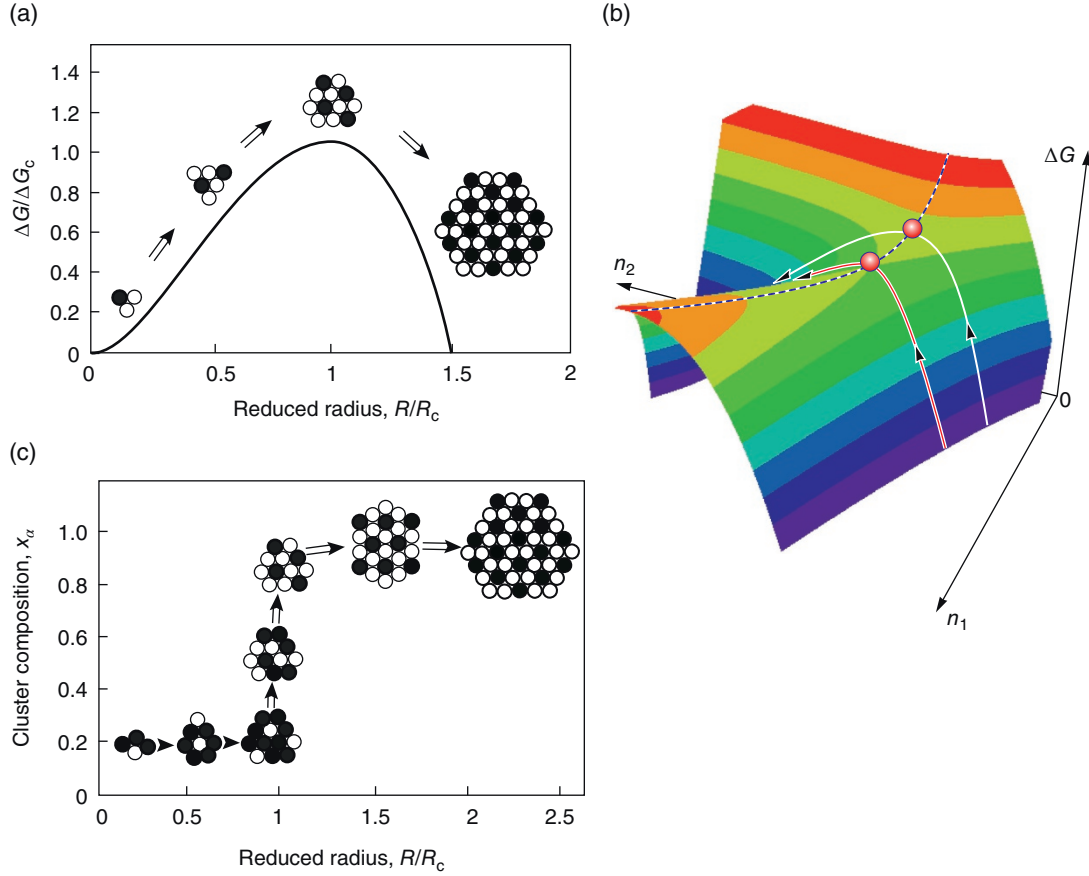


Figure 1 The classical model of nucleation and possible generalizations. (a) With only one parameter employed to describe the state of the cluster. (b) Change of Gibbs free energy in cluster formation when more than one parameter is used. (c) Alternative to the classical scenario of crystallization in multicomponent liquids (See electronic version for color figures).

to the classical picture of phase evolution, which is similar to spinodal decomposition (cf. [3]). In this case, the composition of the critical crystal cluster changes retaining a nearly constant size and only after completion of this process the kinetics are governed by the growth of clusters with a roughly constant composition. In a variety of cases in multicomponent systems [3], the latter path of evolution (Figure 1c) – and not the classical picture (Figure 1a) – dominates phase formation.

Critical clusters do not form according to the predictions (the evolution criteria) of macroscopic thermodynamics, but instead by stochastic thermal fluctuations. According to underlying assumptions of statistical physics, the probability of such fluctuations can be expressed as a function of the minimum work for a reversible thermodynamic process. The minimum work to form a critical cluster is $W_c = \Delta G_c$, where ΔG_c is given by Eq. (2). This quantity, W_c , the work of critical cluster formation, plays a decisive role in nucleation theory. Initially, the nucleation rate is small. Then, after a certain time interval, τ , the so-called time lag for nucleation,

the rate of nucleation, J (i.e. the number of supercritical clusters formed per unit time in a unit volume of the liquid), approaches a constant value, the steady-state nucleation rate, J_s . In an early description of this initial period of nucleation by Zeldovich (cf. [3]), the nucleation rate as a function of time, t , was expressed by the relation

$$J(t) = J_s \exp\left(-\frac{\tau}{t}\right). \quad (3)$$

The initial stage of nucleation observed in experiments is often described by the Collins–Kashchiev relation (cf. [3]):

$$N(t) = J_s \tau \left[\frac{t}{\tau} - \frac{\pi^2}{6} - 2 \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} \exp\left(-m^2 \frac{t}{\tau}\right) \right]. \quad (4)$$

This mathematical equation gives a relation for the number, $N(t)$, of supercritical crystallites as a function on time, t . For longer times than some induction time ($t \gg t_{\text{ind}}$), Eq. (4) can be approximated by

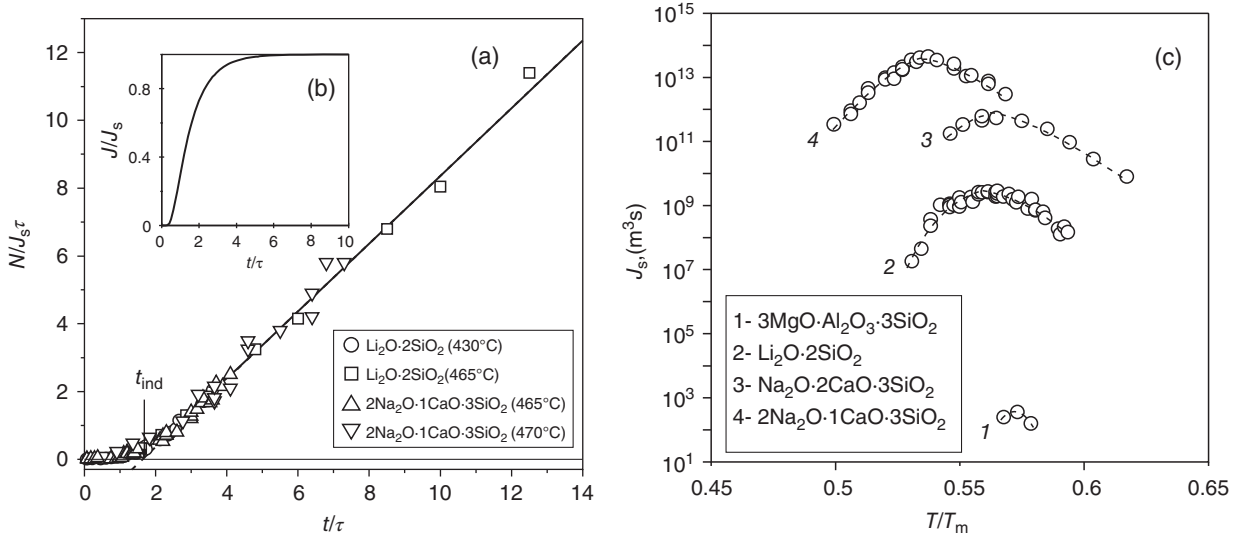


Figure 2 Experimental nucleation rate data for several silicate glasses. (a) Reduced crystal number density, $(N(t)/J_s\tau)$, versus reduced nucleation time, (t/τ) . The solid line is the master curve calculated from Eq. (4). (b) Reduced nucleation rate versus reduced nucleation time calculated from Eq. (4). (c) Experimental steady-state nucleation rate, J_s , versus reduced temperature, T/T_m , for four stoichiometric glasses. T_m is the melting temperature (see [6] for details).

$$N(t) \cong J_s(t - t_{\text{ind}}), \quad t_{\text{ind}} = \frac{\pi^2}{6} \tau. \quad (5)$$

where τ is the nucleation time lag. Over a sufficiently large timescale, Eqs. (3)–(5) approach steady-state nucleation conditions, i.e. $(dN/dt) = J_s = \text{constant}$. With $W_c = \Delta G_c$, the steady-state nucleation rate, J_s , can be written as [3]

$$J_s = J_0 \exp\left(-\frac{\Delta G_c}{k_B T}\right) = J_0 \exp\left(-\frac{W_c}{k_B T}\right), \quad J_0 = \sqrt{\frac{\sigma}{k_B T}} \left(\frac{D}{d_0^4}\right), \quad (6)$$

where D is an appropriately chosen diffusion coefficient and d_0 is a size parameter explained in greater detail below. Experimental results that illustrate the establishment of a steady-state nucleation rate and its dependence on temperature are shown in Figure 2.

For the case shown in Figure 1a (congruent crystallization, assuming that the state of the cluster does not change with size and is the same as that of the newly evolving macroscopic phase), D in Eq. (6) is the diffusion coefficient of the structural building units in the liquid, and d_0 is their diameter. If several components of the liquid diffuse independently, D must be replaced by an effective diffusion coefficient, which is a combination of the partial diffusion coefficients and the concentrations of the different components in the liquid, and d_0 must be replaced by the average size of these independently moving species [3].

In the application of the theory, it is also often assumed that the effective diffusion coefficient can be replaced by

the Newtonian shear viscosity, η , via the Stokes–Einstein–Eyring (SEE) equation [3]:

$$D \cong \frac{k_B T}{d_0 \eta}. \quad (7)$$

However, its applicability to states near and below the glass transition temperature (where homogeneous crystal nucleation is commonly observable) has been questioned even for “one-component” congruent systems, where decoupling of relaxation (expressed by viscosity) and atomic transport (represented by the diffusion coefficient) is frequently reported (e.g. [7]). Application of this expression is even more questionable for multicomponent systems. Another issue is related to the case of highly viscous glass-forming melts, for which a non-Newtonian viscosity should be employed to describe viscous flow [3]. Leaving aside the reservations above, by applying the SEE relationship, one arrives at the following expression for the steady-state nucleation rate:

$$J_s = \frac{\sqrt{\sigma k_B T}}{d_0^5 \eta} \exp\left(-\frac{\Delta G_c}{k_B T}\right). \quad (8)$$

To apply Eq. (8) to the interpretation of experimental data, one has to determine the work of critical cluster formation, $W_c = \Delta G_c$, i.e. to specify the thermodynamic driving force of phase formation, $\Delta\mu$, and the specific interfacial energy, σ in Eq. (2). Assuming that the bulk properties of the crystal clusters are the same as those of the macroscopic crystals, one arrives at the simplest

approximation by a Taylor expansion of $\Delta\mu(T)$ in the vicinity of the melting temperature:

$$\Delta\mu(T) = \Delta h_m \left(1 - \frac{T}{T_m} \right), \quad (9)$$

where Δh_m is the enthalpy of melting per structural unit of the crystal and T_m is the melting temperature (generalizations of this relation can be found in [3]).

Since the interfacial energy of the critical nucleus is not directly measurable, it is normally evaluated using the Stefan–Skapski–Turnbull rule [3]:

$$\sigma = \zeta \frac{q_m}{N_A^{1/3} \nu_m^{2/3}}, \quad q_m = N_A \Delta h_m, \quad (10)$$

via the molar enthalpy of melting, q_m . In Eq. (10), N_A is Avogadro's number, ζ is a factor varying from 0.4 to 0.6, and ν_m is the molar volume. This relation has been widely employed (see [3] and Baidakov et al. [8]). By substituting these relations into the expression for the steady-state nucleation rate, its temperature dependence can be interpreted straightforwardly. The steady-state nucleation rate J_s is equal to zero at $T = T_m$, where $\Delta\mu = 0$, cf. Eq. (9). This rate increases with decreasing temperature because of the decrease in the work of critical cluster formation borne out by Eq. (2), until this trend is overcompensated by the exponential increase in viscosity with decreasing temperature.

When these classical concepts are employed to interpret experimental data, a qualitative and partly quantitative agreement is sometimes found (cf. Figure 2). In most cases, however, the classical approach underestimates the steady-state nucleation rates by 20–55 orders of magnitude, e.g. [6]. In the classical approach, the deviations between experiment and theory can be (artificially) resolved by the introduction of a size dependence of the specific interfacial energy, as discussed by Gibbs [5] and later by others, particularly by Tolman (cf. [3]). But this type of solution gives rise to other problems [6]. Another possible solution, in agreement with results of computer simulations and density functional computations, consists in accounting for the size dependence not only of the surface but also of the bulk properties of the clusters of the newly evolving phases. The bulk properties of the clusters generally depend on their sizes. Hence, the surface properties, including the surface tension, must also be size dependent. Thus, this approach also leads to a size dependence of the surface energy, but the primary variation of the properties of the clusters lies in the size dependence of their bulk properties.

Thermodynamically, one can treat these problems by generalizing the classical Gibbs approach (cf. [3]), which allows for a description of the cluster properties as a

function of size and degree of supercooling. With this new thermodynamic (generalized Gibbs) approach, one concludes that the classical theory – assuming macroscopic bulk properties of the clusters and employing the capillarity approximation for the specific interfacial energy – overestimates the work of critical cluster formation, and hence, underestimates the values of steady-state nucleation rates [3]. Therefore, the classical theory with the “capillarity” approximation may serve as a tool for roughly estimating the nucleation rate curve (i.e. its dependence on temperature and/or pressure), but it must be improved to account for the above-specified effects for a detailed and quantitatively accurate description of the phenomenon.

So far, we have considered the case of crystal nuclei that form evenly within a pure liquid. This mechanism is known as *homogeneous* nucleation. However, nucleation can be readily catalyzed by impurities, such as solid particles embedded in the volume or present on the external surface of glasses. Nucleation originating at such preferential sites is denoted as *heterogeneous* (e.g. [3, 9]) and can be described by the theoretical concepts outlined above if the work of critical cluster formation for homogeneous nucleation, W_c , is replaced by $W_c \Phi$. Here, $\Phi \leq 1$ is the nucleating activity of the heterogeneous nucleation core, and its value depends on the mechanism of nucleation catalysis. As a rule, heterogeneous nucleation dominates at small supercooling because of the lower work of critical cluster formation than that of homogeneous nucleation. At high supercooling, homogeneous nucleation dominates due to the much larger number of sites (all “molecules” of the system) where homogeneous nucleation may proceed.

The reader should note that, in certain cases, the evolution of the new phase may not proceed via the saddle shown as a dark curve in Figure 1b (in red in the colored version) but via a ridge trajectory indicated by a light curve in Figure 1b (in yellow in the colored version), if such a trajectory is kinetically favored. This type of behavior may be expected to occur in crystallization occurring at large degrees of supercooling because of the disordered and nonstoichiometric nature of the crystals that precipitate in the early stages.

Frequently, several different stable or metastable phases may be formed at some given initial state of the supercooled liquid. As Ostwald suggested (cf. [3]), in such cases the most favorable stable phase is not formed immediately. Instead, the final stable phase is reached via several stages in which different metastable phases are formed until the most stable phase is developed: this is the so-called Ostwald's rule of stages or Ostwald's step rule. As first proposed by Stranski and Totomanov (cf. [3]), this evolution path can also be explained by kinetic considerations.

3 Basic Models of Crystal Growth in Supercooled Liquids

It is now generally accepted that the properties of the crystal–liquid interface have a decisive influence on the kinetics of crystallization. Theoretical treatments of crystal growth have therefore focused closely on the interfacial structure and its effect on crystallization. With the assumption of congruent crystallization, three standard models have been developed for treating crystal growth theoretically (e.g. [10, 11]). These models are described briefly below:

- i) *Normal growth*: The interface is pictured as rough at an atomic scale. Growth takes place at step sites, which represent a sizable fraction (0.5–1.0) of the interface. Assuming that this fraction does not change appreciably with temperature, the growth rate, $u(T)$, can be expressed as

$$u = f \frac{D}{4d_0} \left[1 - \exp \left(- \frac{\Delta\mu}{k_B T} \right) \right], \quad (11)$$

where f is close to unity and $\Delta\mu$ is treated as a positive quantity.

- ii) *Screw dislocation growth*: This model assumes the interface is smooth but imperfect at an atomic scale. Growth takes place at a few step sites provided by screw dislocations that intersect the interface. The growth rate is still given by Eq. (11), where f is now the fraction of preferred growth sites (on the dislocation ledges) at the interface. In this case, f is given approximately by $f \simeq (T_m - T)/(2\pi T_m)$ [7]. More generally, according to Jackson [10], $f = (\Delta s_m/k_B)\xi$ holds, where Δs_m is the entropy of fusion per particle and ξ is the number of nearest-neighbor sites in a layer parallel to the surface divided by the total number of nearest-neighbor sites. Factor ξ is the largest for the most closely packed planes of the crystal, for which it is approximately equal to 0.5.

For $f < 2$, the minimum free energy configuration corresponds to half the available sites being filled and represents an atomically rough surface. In contrast, for $f > 2$, the lowest free energy configuration corresponds to a surface where few sites are filled and a few units are missing from the completed layer, which represents an atomically smooth interface. Hence, for materials with $\Delta s_m < 2k_B$, the most closely packed interface planes should be rough. For materials with $\Delta s_m > 4k_B$, the most closely packed surfaces should be smooth, the less tightly packed surfaces rough, and the growth anisotropy rate large.

- iii) *Surface nucleation or two-dimensional growth*: According to this model, the interface is smooth

and perfect at an atomic scale and thus free of intersecting screw dislocations and growth sites. Growth then takes place by the formation and growth of new two-dimensional nuclei at the interface. In this case, the growth rate is expressed by

$$u = C_3 \frac{D}{4d_0^2} \exp \left(- \frac{C_2}{T\Delta T} \right), \quad (12)$$

where C_2 and C_3 are parameters that determine the time required for the formation of the two-dimensional nucleus relative to that required for its propagation across the interface, respectively.

Possible growth modes are illustrated in Figure 3. Similarly to nucleation, the interplay between increasing driving force for crystallization, $\Delta\mu$, and decreasing diffusion coefficient (or increase in viscosity) with decreasing temperature results in a maximum of the crystal growth rates. This maximum is located at higher temperatures than that of the maximum of the steady-state nucleation rate shown in Figure 2c.

There are also other growth modes, which are rate limited not by processes at the liquid–crystal interface but by mass transport toward the interface. A specific example is a diffusion-limited segregation, which is of particular importance in multicomponent systems. Accounting for size effects on the growth kinetics, one can express the rate for such a growth mode as (e.g. [11, 12])

$$\frac{dR}{dt} = \frac{B}{R} \left(\frac{1}{R_c} - \frac{1}{R} \right), \quad (13)$$

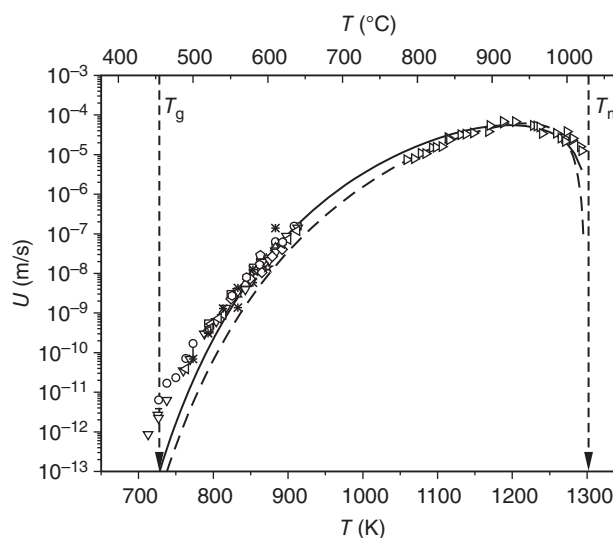


Figure 3 Crystal growth rates for $\text{Li}_2\text{O}-2\text{SiO}_2$ glasses obtained by different authors. The lines correspond to the screw dislocation mechanism (full curve) and two-dimensional surface nucleated growth (dashed curve) [7].

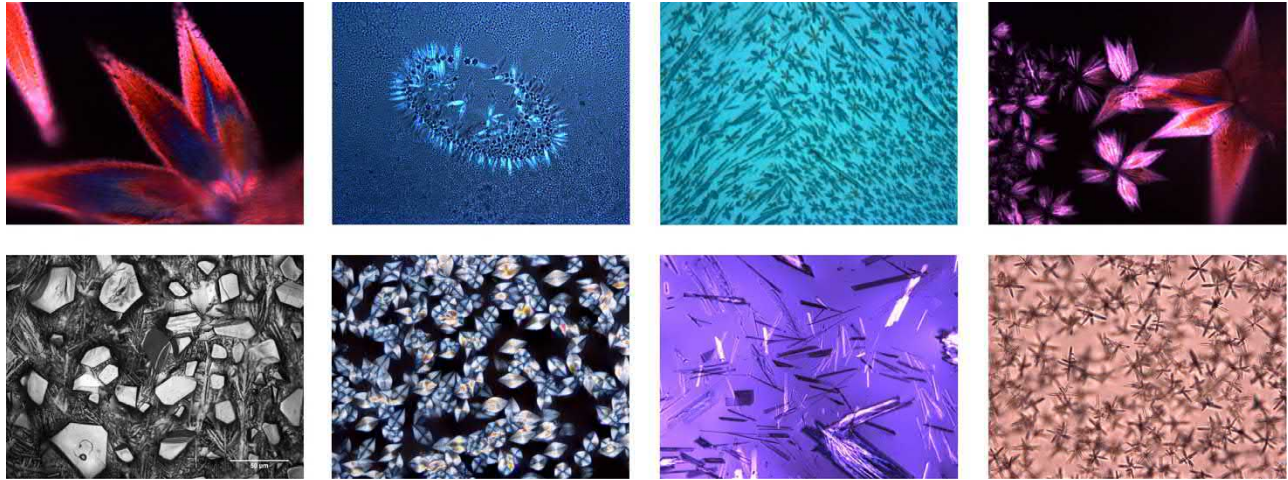


Figure 4 Crystal morphologies formed by nucleation and growth in glass-forming liquids as observed by optical microscopy (crystal sizes from 5 to 100 μm). From top left to bottom right: (i, ii, iv) LS crystals nucleated on defects of a $\text{CaO-Li}_2\text{O-SiO}_2$ glass surface during its preparation via melting–cooling. (iii) Crystallization propagating from the surface toward the center of a $\text{CaO-Li}_2\text{O-SiO}_2$ glass specimen; lithium metasilicate crystals nucleated on two perpendicular surfaces and grew toward the sample center. (v) Surface of a $\text{CaO-Li}_2\text{O-SiO}_2$ glass sample after cooling a melt in a DSC furnace; the large-faceted and needle-like crystals are calcium and lithium metasilicates, respectively. (vi) Internal crystallization in a Ti-cordierite glass; pure stoichiometric cordierite ($2\text{MgO-2Al}_2\text{O}_3\text{-5SiO}_2$) glass underwent only surface nucleation, but the same glass doped with more than 6 mol % TiO_2 shows internal crystallization of μ -cordierite. (vii) Needle-like crystals in $\text{CaO-Li}_2\text{O-SiO}_2$ eutectic glass formed by internal crystallization in the temperature range between the *solidus* and the *liquidus*; these wollastonite crystals appear on the cooling path. (viii) Starlike NaF crystals inside a PTR glass (treatment at a high temperature near the solubility limit).

where B is a combination of parameters describing the liquid under consideration, being proportional to the effective diffusion coefficient governing the rate of supply of the different components to the growing or dissolving cluster.

Equation (13) and its modifications for other growth modes serve as a basis for the theoretical description of the competitive growth of clusters denoted as coarsening or Ostwald ripening. In these late stages of phase formation, larger clusters may grow further only when subcritical crystals are dissolved. The theoretical description of this process was first developed by Lifshitz and Slezov (cf. [11]). Today it is often referred to as the Lifshitz–Slezov–Wagner theory. This theory provides expressions for the average size, $\langle R \rangle$, and the number, N , of supercritical clusters in the system as a function of time. For diffusion-limited growth (Eq. (13)), one obtains

$$\langle R \rangle^3 \propto t, \quad N \propto \frac{1}{t}. \quad (14)$$

An account of the effect of elastic stresses on coarsening, which leads to qualitative modifications of the coarsening behavior, is reviewed in [3, 12].

The above relationships allow one to describe the growth of crystals with smooth planar or spherical interfaces advancing in the liquid. However, more complex growth patterns do exist, and more complex models of growth are required to properly take into account

possible interfacial instabilities, surface roughening, or other growth modes such as diffusion-limited aggregation [11]. With such complex growth modes, a variety of intricate and beautiful crystal shapes may evolve, some of which are illustrated in Figure 4.

4 Overall Crystallization and Glass-forming Ability: The Johnson–Mehl–Avrami–Kolmogorov Approach

The overall crystallization of supercooled liquids occurs by a combination of crystal nucleation and growth. The kinetics of such processes is usually described by a theory independently derived between 1937 and 1941 by Johnson, Mehl, Avrami, and Kolmogorov [13–17] (JMAK theory). In this approach, the evolution of the total amount of crystalline phase is described as a function of time, accounting simultaneously for nucleation and growth. The basic equations of this approach can be developed as follows.

Let us assume that, in a time interval $dt'(t', t' + dt')$, a number $dN(t') = J(t')[V - V_n(t')]$ of clusters of critical size is formed in the volume $[V - V_n(t')]$. Here, V is the initial volume of the glass-forming melt and $V_n(t')$ the volume already crystallized at time t' . These clusters grow and, at time t , occupy a volume

$$dV_n(t, t') = \omega_n J(t') (V - V_n(t')) dt' \left(\int_{t'}^t u(t'') dt'' \right)^n, \quad (15)$$

where ω_n is a shape factor and the integral term describes the growth of the $dN(t')$ clusters formed at t' until time t , i.e. in the time interval $(t-t')$, the exponent n is the number of independent spatial directions of growth. Introducing the ratio, $\alpha_n(t) = (V_n(t)/V)$, between the current volume of the crystalline phase versus the initial volume of the glass-forming melt, one has

$$d\alpha_n(t, t') = \omega_n J(t') (1 - \alpha_n(t')) dt' \left(\int_{t'}^t u(t'') dt'' \right)^n. \quad (16)$$

Integration, i.e. taking the sum over all the time intervals dt' in the range of $(0, t)$, yields

$$\alpha_n(t) = 1 - \exp \left(\omega_n \int_0^t J(t') dt' \left(\int_{t'}^t u(t'') dt'' \right)^n \right). \quad (17)$$

Provided the nucleation and growth rates are both constant, one reaches as a special case

$$\alpha_n(t) = 1 - \exp \left(- \frac{\omega_n}{(n+1)} J u^n t^{(n+1)} \right). \quad (18)$$

Conversely, if a number N_0 of supercritical clusters is formed immediately at time $t = 0$, growing in n independent spatial directions, one arrives instead at

$$\alpha_n(t) = 1 - \exp(-g N_0 u^n t^n). \quad (19)$$

The analysis of the time dependence of the $\alpha_n(t)$ -curves thus leads one to the specification of nucleation and growth kinetics.

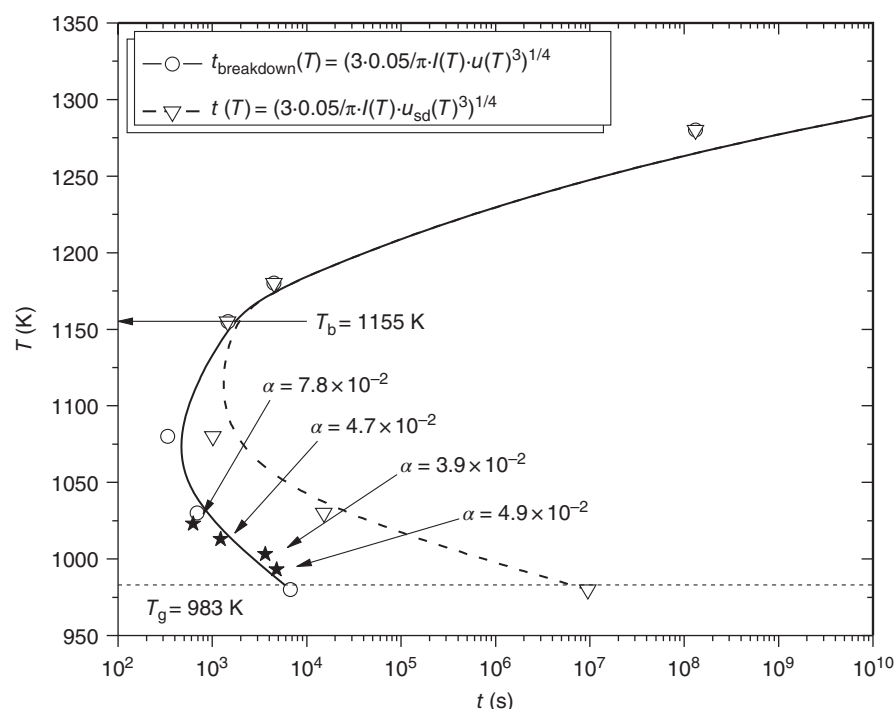
The JMAK theory has been employed in numerous studies to analyze experimental data and determine the degree of crystallinity as a function of time in both isothermal and non-isothermal heat treatments of glass systems. Emphasis has usually been given to the determination of the so-called Avrami coefficient $m = n + 1$ obtained from the slopes of experimental $\ln[1 - \alpha]^{-1}$ versus $\ln(t)$ plots. An overview of various nucleation and growth mechanisms and the resulting values of the Avrami coefficient are given in [3]. However, there is some uncertainty in such analyses, because different combinations of nucleation and growth laws may lead to the same Avrami coefficient. For this reason, a separate investigation of the growth kinetics may be required to reach definite conclusions [14].

It is important to underline that the JMAK theory, as given by Eqs. (18) and (19), does not apply to non-isothermal processes. These two equations are derived from the assumption of constant nucleation and growth rates, which are not achieved in non-isothermal processes. Therefore, in non-isothermal cases, the general relationships, Eqs. (16) and (17), must be employed to describe overall crystallization. This requires taking into consideration not only thermal nucleation (formation of supercritical clusters due to thermal fluctuations at given values of critical cluster size and thermodynamic barrier) but also athermal nucleation (i.e. the change in the number of supercritical clusters due to the variation of the critical cluster size resulting from the change in temperature).

Such considerations must also be taken into account when the JMAK formalism is employed to determine whether a liquid will transform into a glass upon cooling or whether it will crystallize. Following Uhlmann (cf. [10]), one can consider a supercooled frozen in liquid as a glass if, after vitrification, the volume fraction of the crystal phase does not exceed a certain value of, say, 10^{-6} (the detection limit by microscopy). Using appropriate expressions for nucleation and growth rates, one can then compute (through Eq. (18) for isothermal conditions) the time required to reach the volume fractions thus defined. In this way, one arrives at the so-called $T(\text{ime})T(\text{emperature})T(\text{ransformation})$ curves (TTT curves) exemplified in Figure 5 (cf. also [18] and figure 10.8 in [3]). These curves give some insight into the characteristic timescales required to prevent measurable crystallization effects. One should keep in mind, however, that these curves overestimate the critical cooling rates for glass formation by about one order of magnitude because, as mentioned earlier, crystallization upon cooling proceeds under non-isothermal conditions.

Using experimental nucleation and growth rate data, Rodrigues and Zanotto [19] calculated TTT curves for different isothermal and non-isothermal crystallization situations. They also accounted for the breakdown of the SEE equation at a temperature T_b (somewhat higher than T_g) where the effective diffusion coefficient that controls crystal growth decouples from the value of diffusivity calculated by the SEE equation (Eq. (7)). In Figure 5 we show an example of such a curve for a stoichiometric $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{SiO}_2$ glass, which undergoes copious internal homogenous crystal nucleation. The agreement with experimental data (which, in this case, were also obtained in isothermal conditions) is quite impressive, indicating that the JMAK equation is accurate if all the assumptions involved in its derivation are met.

Figure 5 Simulated TTT curves for a $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{SiO}_2$ glass with crystallized volume fraction $\alpha = 0.05$ using, in one approach, the screw dislocation growth model both above and below T_b (t_{sd} – dashed line), and in the other the Arrhenius equation below T_b ($t_{\text{breakdown}}$ – solid line). Experimental data points (black stars) obtained at 993, 1003, 1013, and 1023 K [15].



5 Perspectives

Significant advances in the understanding and control of crystal nucleation and growth processes in glass-forming liquids have been achieved in the last five decades. It is now well-established that almost all materials can vitrify when subjected to sufficiently fast cooling from the liquid state. Thus, novel materials, such as metallic and chalcogenide glasses with unusual properties, have been obtained successfully by very fast quenching. Also, controlled, catalyzed internal crystallization of specific glasses has led to a variety of advanced glass ceramics that are now manufactured commercially. More profound insights into glass crystallization processes, such as precise predictions of nucleation and growth rates and critical cooling rates for glass formation, based solely on materials properties, will depend critically on new developments in nucleation and growth theories and computer simulations.

Despite the many advances achieved in understanding crystallization processes in glasses, some problems remain open. Among the most important, we remark the following: (i) specification of the bulk (structure, composition, density) and surface properties of the critical nuclei and sub- and supercritical crystals as a function of their sizes; (ii) description of the temperature dependence of the crystal nucleus–liquid interfacial energy and the degree of validity of the Stefan–Skapski–Turnbull equation; (iii) applicability of the SEE (viscosity) relationship in calculating the effective diffusion coefficients that control crystal nucleation and crystal growth; (vi) a clear

understanding of the causes of the breakdown of the SEE equation reported for crystal growth somewhat above T_g ; (v) unveiling the cause of the reported breakdown of the CNT in describing the temperature dependence of experimental nucleation rates below T_g ; (vi) a deeper understanding of the relationship, if any, between the molecular structure of glass-forming melts and the nucleation and growth mechanisms [20]; (vii) the relation between the sizes of supercritical nuclei vis-à-vis the sizes of cooperatively rearranging regions (CRR) of the configurational entropy theory and the domains of heterogeneous dynamics (DHD) envisaged in the structure of viscous liquids [21]; and (viii) comparison of the estimated (by extrapolation) structural relaxation time and the characteristic time for crystallization of glass-forming liquids at the (predicted) Kauzmann temperature, T_K [22, 23]. Such a comparison could resolve the paradox, following Kauzmann's suggestion of the possibility that the putative state of negative entropy may never be reached because crystallization would always intervene before structural relaxation. A detailed analysis of the Kauzmann paradox and his hypothesis about the existence of a kinetic spinodal has been performed recently [24]. In addition, the ratio of the mentioned times scales is of considerable importance concerning the problem whether some basic assumptions of CNT concerning the methods of determination of the thermodynamic driving force and the surface tension hold or not for crystallization under time-dependent temperature and/or pressure [25]. All these problems, in addition to several others not

mentioned here, such as the development of novel glasses and glass ceramics, having exotic, unusual compositions and combination of properties, serve as great incitement for glass crystallization being a very active research topic!

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Table of Symbols

ΔG	Gibbs free energy difference
R	cluster radius
A	nucleus surface area
N	number density of supercritical crystallites
$\Delta\mu$	chemical potential difference
μ_l	the chemical potentials per particle in the liquid
μ_{cr}	the chemical potentials per particle in the crystal
σ	surface free energy
c_α	particle number density in the crystal cluster
P	pressure
T	temperature
G	Gibbs free energy
R_c	critical radius
ΔG_c	change in the Gibbs free energy for a critical cluster
n_i	number of particles of the different components in the cluster
W_c	work of critical cluster formation
τ	time-lag in nucleation
J	rate of formation of supercritical clusters
J_s	steady-state nucleation rate
t	time
n_c	number of particles in a cluster of critical size
τ_R	Maxwellian relaxation time
η	Newtonian viscosity
t_{ind}	induction time
dN	change of number of clusters of critical size

dt	time interval
k_B	Boltzmann's constant
D	diffusion coefficient
d_0	diameter
T_m	melting temperature
Δh_m	heat of melting of one crystal phase particle
q_m	heat of melting
N_A	Avogadro's number
ζ	correction factor
f	fraction of preferred growth sites
Δs_m	entropy of melting
C_2, C_3	parameters determining the time required for the formation of the two-dimensional nucleus and for its propagation across the interface, respectively.
B	combination of parameters proportional to the effective diffusion coefficient
$\langle R \rangle$	average size of the nuclei
dt'	time interval
V	volume
V_n	volume crystallized
ω_n	shape factor
$\alpha_n(t) = (V_n(t)/V)$	time-dependent crystallized fraction
N_0	number of supercritical clusters
n	number of independent spatial directions
T_b	Stokes–Einstein breakdown temperature
T_g	glass transition temperature
T_K	Kauzmann temperature
Φ	catalytic activity factor of a heterogeneous nucleation core

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5.5

Solubility of Volatiles

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1 Introduction

Even though a few hundred ppm of dissolved water may affect to a measurable extent physical properties of SiO₂ glass [1], volatile concentrations higher than 1% usually are required to exert significant effects in oxide glasses and melts. Because pressures of the order of 100 Pa are typically needed to achieve a solubility of 1 wt %, dissolution of volatiles remains a difficult and expensive task, which is hampering any practical application of the materials produced. As a result, volatile solubilities and their effects on physical properties have been mostly studied to understand the fundamental role they play in geological processes. The relevant systems are then made up of silicates along with the halogens F₂ and Cl₂, the He–Xe series of noble gases, and a number of species in the system C–O–H–N–S, namely, H₂O, H₂, CO₂, CO, CH₄, N₂, NH₃, SO₂, S, and H₂S. To illustrate in this chapter the manner in which the structure and physical and chemical properties of silicate glasses and melts change upon volatile dissolution, we will review experimental data from systems that are comparatively simple (unary to quaternary) with extrapolation to more complex chemical environments when appropriate.

2 Principles and Concepts

2.1 Reactive and Nonreactive Solubility

The solubility of volatiles in a silicate structure and its effects on it depend on gas and silicate compositions

together with temperature, pressure, and redox conditions (as generally specified by oxygen or hydrogen fugacity). The sensitivity to the interplay of these conditions is illustrated by the fact that, under reducing conditions, species such as CH₄ and NH₃ may form in the presence of hydrogen, whereas formation of carbides and nitrides takes place instead if hydrogen is lacking in the melt. These examples also illustrate the generally *reactive* nature of volatile dissolution, where the volatile species forms chemical bonding with the silicate structure and in the process affect the properties of the material. Examples include H₂O, which forms OH groups. The CO₂ and SO₂ form CO₃ and SO₄ groups, respectively, by sharing oxygen with the silicate. In other structural interactions, oxygen in the silicate structure can be replaced with functional groups such as CH₃ from methane and NH₂ from ammonia and S-bearing groups from H₂S. Exchange of oxygen in the silicate tetrahedra with C, N, or S can also occur. In addition, water, carbon dioxide, ammonia, and methane can dissolve either as molecular or *nonreactive* molecular species together with a reactive portion (e.g. OH groups and H₂O) whose proportions also depend on all intensive thermodynamic variables. Species that dissolve only in molecular and nonreactive form at noble gases and N₂.

Although it is possible to dissolve volatiles in glasses, most experimental studies have been performed on melts, which were then temperature-quenched to glass to ascertain that an equilibrium state was actually reached and to give sound basis to thermodynamic modeling of the solution process. In this chapter we will thus restrict ourselves to these conditions. It is implied, therefore, that the volatile species have equilibrated with the silicate structure under specific temperature, pressure, and redox conditions before the melt is quenched to a glass. Two kinds of experiments must be further distinguished depending on whether the melt is undersaturated or saturated with

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the volatile of interest. In the latter case, equilibration between the volatile in the melt and in a coexisting gas phase is of course necessary.

2.2 Glass Versus Quenched Melt

The physics of the glass transition is discussed elsewhere (Chapter 3.3). Here, we will address only how, or the extent to which, volatiles dissolved in melts may be quenched in the glass structure and whether, or the extent to which, the structure of volatile components in glass is a viable representation of the structural environment of volatile-containing silicate melts.

The solubility in melts of the individual volatile species considered in this chapter differs significantly, is slightly temperature dependent, and is often a pronounced function of pressure (Table 1). As a result, a melt must be decompressed and cooled down from the equilibrium conditions either to synthesize a glass with a desired volatile content or in order to examine a volatile-bearing glass as a proxy for its melt. In order to retain the volatile content in the quenched glass of the high-temperature/pressure melt, the quenching rate must exceed the rate at which volatiles may exsolve. The exsolution rate depends primarily on the diffusivities of volatiles and the nucleation rate of gas bubbles in the cooling melt. Furthermore, equilibria between different functional groups of volatile species in principle depend on both temperature and pressure. Therefore, when studying volatiles in glass, it must be kept in mind that volatile contents and their solution mechanism may have been affected by the glass-forming process.

2.3 Intensive Variables (Pressure, Temperature, Redox Conditions)

A description of the principles that govern silicate–volatile equilibria at temperatures above the liquidus is useful for

Table 1 Solubility (mol %) of H₂O, CO₂, and SO₂ in NaAlSi₃O₈ composition melt near 1500 °C as a function of pressure (GPa).

Pressure (GPa)	H ₂ O	CO ₂	SO ₂
0.5	59	4.2	1.6
1.0	78	6.1	2.1
1.5	82	7.6	2.5
2.0	84	8.2	2.8
2.5		9.0	3.1
3.0		9.6	3.3

Source: data summary from [2].

understanding relationships between composition, temperature, and pressure (Figure 1). At a given pressure, there exists a temperature range from the solidus (a eutectic point is used for this illustration in Figure 1) to a critical point (*c. p.*), where a melt is saturated with respect to the volatile component of interest. In this temperature range, a solvus separates the stability field of volatile-saturated melt+volatile-rich fluid and the boundary between volatile-rich fluid and volatile-saturated melt. The former boundary defines the solubility of the volatile component(s) in the melt. At temperatures above the critical point, there is no distinction between melt and fluid. The width and height of the solvus (in the temperature–composition space illustrated in Figure 1) diminish with increasing pressure.

The solubility of volatiles in silicate melts is sensitive to pressure. As already stated, it often can increase from only a few hundred ppm at ambient pressure to several mol % at several hundred MPa. Water is an example of such a component. The effects of temperature are generally smaller, but remain significant, and can also be dependent on pressure. As for redox conditions, they also affect the silicate–volatile phase relations through their influence on volatile speciation. For example, the solubility of CH₄ is less than half of that of CO₂ for a given silicate composition, temperature, and pressure. Ammonia (NH₃) solubility, on the other hand, can be several times higher than that of N₂.

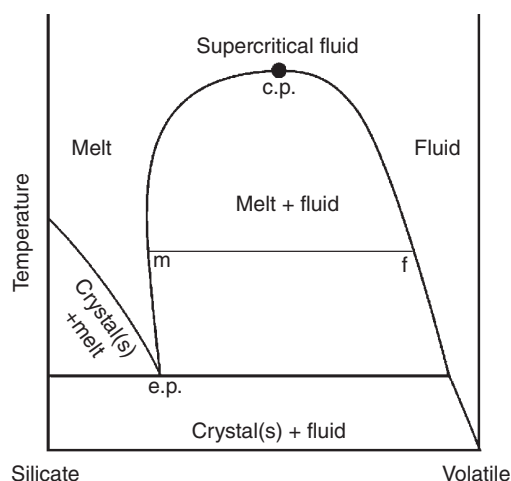


Figure 1 With water as an example, schematic representations of phase relations in silicate + volatile systems. Only a simple eutectic defines the minimum temperature of melting and a simple solvus separating volatile-bearing melt from silicate-bearing fluid, which determines the solubility of volatile component as a function of temperature at given pressure. The width of the solvus depends on pressure and silicate composition and can also vary with redox conditions.

2.4 Composition

Silicate and gas composition affect solubility and solubility mechanisms of volatiles in melts. When a multicomponent gas coexists with a melt with which it is completely miscible, the gas composition is enriched in the component that is least soluble in the melt. Examples are silicate–H₂O–CO₂ mixtures because the solubility of CO₂ in silicate melts is only a small fraction of that of H₂O (see Table 1). When gas speciation is redox dependent, the fractionation of the components between the melt and coexisting gas will also vary with redox conditions. The activity–composition relations in the gas phase also can play an important role.

As defined above, volatile solution is nonreactive when it is governed by the availability and dimensions of the cavities (structural locations) in the structure that are occupied by the volatile molecules. Then the degree of melt polymerization (NBO/Si; see Chapter 2.6) is the most important variable affecting this solubility because the more polymerized a silicate melt and glass, the greater the availability of cavities thanks to the larger proportion of rings made up of SiO₄ tetrahedra. An example is silica-rich compositions where Q⁴ species are the dominant structural components (three-dimensionally interconnected network of silicate tetrahedra). Moreover, for a given silicate melt, temperature, and pressure, the solubility increases as the atomic or molecular radius of the nonreactive element or compound decreases. Examples are noble gases (He–Xe) and N₂.

When the dissolved volatile component interacts chemically with the silicate, its solubility depends on the availability of bridging and nonbridging oxygen and on the electronic properties of network-forming and network-modifying cations. When cations serve to charge-balance tetrahedrally coordinated Al³⁺, the nature of the charge-balancing cations also affects solubility and solution mechanisms. In addition, silicate composition affects the temperature- and pressure-dependent solubility of the volatile components such as OH[−], CO₃^{2−}, SO₃^{2−}, NH₂[−], and CH₃.

3 Reactive Volatiles in Silicate Glass and Melt

Except noble gases and molecular nitrogen, all the volatiles considered in this chapter are reactive. Other volatiles may dissolve in a manner that includes both reactive and nonreactive species (e.g. molecular H₂O vs. OH groups and CO₂ vs. CO₃ groups).

3.1 Hydrous Glass and Melt

Among the volatiles discussed in this chapter, dissolved water has the most profound influence on glass and melt

structure and properties. Its solubility in silicate melts is also greater than that of any of the other volatiles except, perhaps, fluorine.

3.1.1 Solubility and Solution Mechanisms

When quenched from a hydrous melt, glasses have water contents varying from a few hundred to a few thousand ppm at ambient pressure to several tens of mol % at pressures in the MPa–GPa range. In silicate–H₂O systems, there exists a maximum pressure and temperature above which complete water miscibility obtains, which defines the critical point (c.p., shown schematically in Figure 1). The pressure/temperature coordinates of the critical point are sensitive functions of silicate composition and range from about 1 GPa/600 °C for Na silicates to >5 GPa/>1100 °C for Mg silicates. The electronic properties (ionization potential) of the metal cation appear the most important variable affecting the pressure/temperature coordinates of the critical point.

Below the critical point (c.p. in Figure 1), the solubility of H₂O is a strongly nonlinear and positive function of total pressure and a positive or negative function of temperature depending on pressure and silicate composition (Figure 2). In addition, water solubility strongly depends on silicate composition, being a negative function of Al/(Al+Si) and of the ionization potential, Z/r^2 , of the metal cation (Z : formal electrical charge, r : ionic radius). In

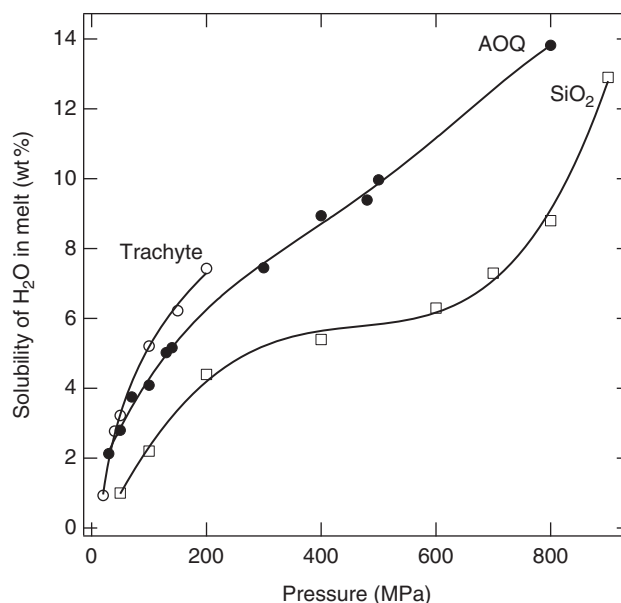
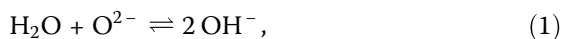


Figure 2 Isothermal solubility of pure water in various silicate melts as a function water pressure, $P_{\text{H}_2\text{O}}$. Trachyte (data from [3]) a natural magma composition ($\text{SiO}_2 = 61.71$ wt %, $\text{Al}_2\text{O}_3 = 18.56$, $\text{FeO} = 3.17$, $\text{MnO} = 0.27$, $\text{MgO} = 0.23$, $\text{CaO} = 1.64$, $\text{Na}_2\text{O} = 6.11$, $\text{K}_2\text{O} = 7.09$), AOQ (data from [4]) are for a model composition ($\text{SiO}_2 = 76.14$ wt %, $\text{Al}_2\text{O}_3 = 13.53$, $\text{Na}_2\text{O} = 4.65$, $\text{K}_2\text{O} = 5.68$). Solubility data for SiO_2 melt are from [5].

contrast, water solubility in aluminosilicate melts increases with the electronegativity of the cation that charges compensate Al^{3+} in tetrahedral coordination (see Chapter 2.6).

Under equilibrium conditions the high-pressure and temperature solution mechanisms of water vapor in silicate melts have been described by the expression



where the abundance ratio of molecular water, H_2O° , to structurally bound OH groups, $\text{H}_2\text{O}^\circ/\text{OH}$, varies because the proportion of molecular H_2O increases with increasing total water content (Figure 3). For glasses, the $\text{H}_2\text{O}^\circ/\text{OH}$ ratio is insensitive to temperature, but above the glass transition, equilibrium (1) shifts to the right with a ΔH around 30 kJ/mol.

The O^{2-} in Eq. (1) is the structural link between the water speciation and silicate structure. In its simplest form, such as in the system $\text{SiO}_2\text{--H}_2\text{O}$, the OH groups are formed by breaking the oxygen bridges in the three-dimensional network structure of silica glass and melt:



where SiO_2 is represented as Q^4 and $\text{Q}^3(\text{H})$ denotes a Q^3 species with protons serving as network-modifying cation (see Chapter 2.4 for discussion of Q^n species in silicate glasses). In chemically more complex silicate glasses, OH groups also bond with Al^{3+} , alkali metals, and alkaline

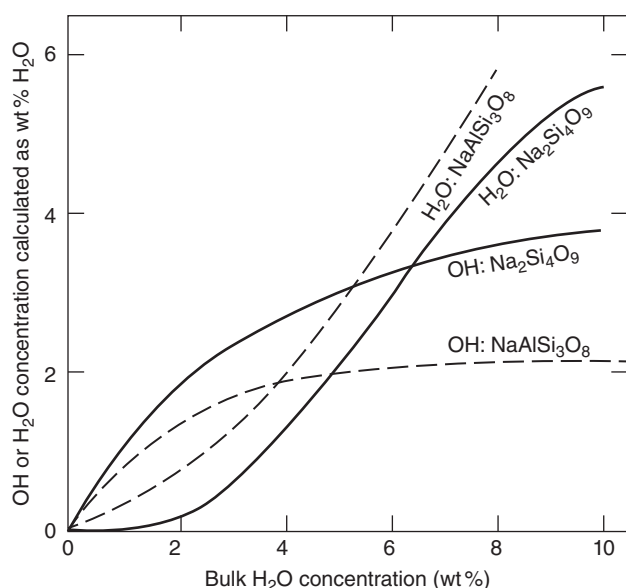


Figure 3 Speciation of water as molecular H_2O and OH groups in melts of compositions indicated as a function of bulk (total) water content. Data for $\text{Na}_2\text{Si}_4\text{O}_9$ glasses quenched from 1100 °C at 200 MPa (data from [6]) and for $\text{NaAlSi}_3\text{O}_8$ glass quenched from 1400 °C and 1.5–2.0 GPa (data from [7]).

earths, thus creating more complex relations between the structure, composition, and solubility and solution mechanisms of water in silicate melts and glasses (Figure 2).

3.1.2 Structure–Property Relations

Transport, volume, and thermodynamic properties of silicate glasses and melts significantly depend on water content because of the alteration of the silicate structure caused by formation of OH groups. Viscosity, electrical conductivity, and diffusion are quite sensitive, so about 1 wt % water, for example, can lower melt viscosity by several orders of magnitude. Increasing water content also results in increasing configurational entropy, lower glass transition temperature, and lower melting temperatures (see data review in [1], Chapter 14). These variations are partly due to formation of depolymerized Q^n species upon water dissolution. Similar reasoning explains increased diffusivity of water at higher water contents.

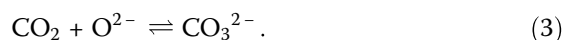
3.2 Oxidized Carbon (CO_2)

Carbon is the second most abundant element of the C–O–H–N–S system in Earth. In the C–O–H subsystem, CO_2 at the temperature of molten silicates is stable down to oxygen fugacities about three to four orders of magnitude lower than that of air.

3.2.1 Solubility and Solution Mechanisms

The solubility of CO_2 in silicate melts at ambient pressure is lower than 0.1 wt %, but it increases rapidly with pressure and also varies with the water content of the melt sometimes with a maximum CO_2 solubility at intermediate $\text{CO}_2/\text{H}_2\text{O}$ abundance ratios. The solubility of CO_2 is less than 10 % of that of water under otherwise identical silicate composition, temperature, and pressure, and it depends more strongly on melt composition. Of particular importance are polymerization (NBO/T) and the electronic properties of the network-modifying cations (alkali metals and alkaline earths) (Figure 4). There is a positive correlation of CO_2 solubility with NBO/T whether in chemically simple or more complex silicate compositions [9]. The $\text{Al}/(\text{Al}+\text{Si})$ ratio and metal cation types and proportions also affect the solubility.

From vibrational (Raman and FTIR) and carbon-13 NMR spectroscopy of quenched, CO_2 -saturated melt (glass), carbon dioxide is found to dissolve in the form of CO_3^{2-} complexes and molecular CO_2 . The expression, which is analogous to that describing the $\text{H}_2\text{O}/\text{OH}$ relationships in silicate glasses and melts (Eq. (1)), is



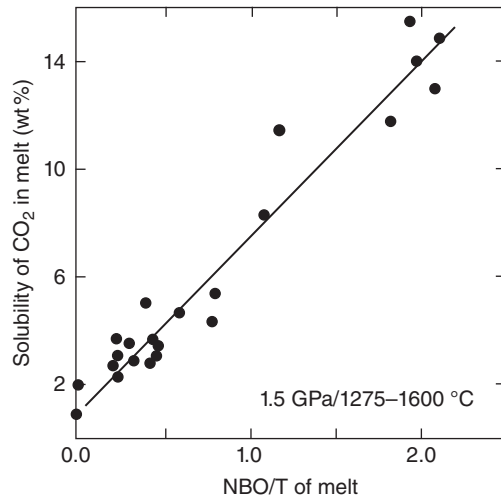
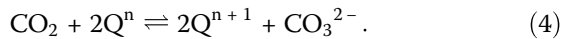


Figure 4 Solubility of carbon dioxide in CaO–MgO–Al₂O₃–SiO₂ melts determined in glass quenched from 1275 to 1600 °C at 1.5 GPa as a function of the degree of polymerization of the melt (NBO/T, where T = Al³⁺ + Si⁴⁺) (data from [8]).

Here, as for water, the O²⁻ is the link to the silicate structure. This link can be replaced by Qⁿ-species equilibria to yield



This equilibrium is sensitive to bulk composition and shifts to the right with increasing metal oxide/SiO₂ and Al/(Al+Si) ratio ([1], Chapter 16). In mixed CO₂/H₂O environments, decreasing CO₂/H₂O in coexisting gas also shifts this equilibrium to the right. Available information indicates that at temperatures above the glass transition, equilibrium (3) shifts to the left with increasing temperature and decreasing pressure (Figure 5).

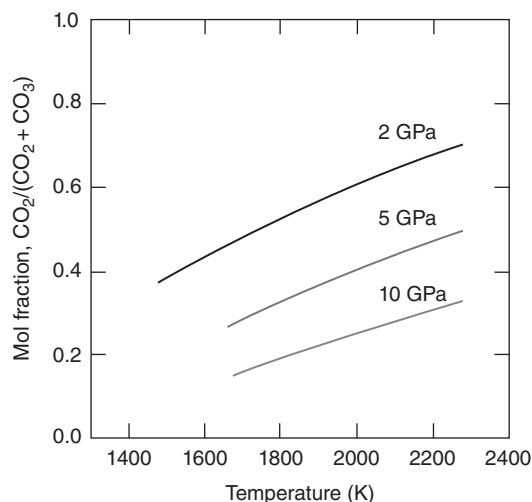


Figure 5 Calculated proportion of molecular CO₂ and carbonate groups, CO₃, in melt of basalt composition as a function of temperature and pressure (calculations by [10]). See also Chapter 2.6 for further discussion of basalt composition.

3.2.2 Structure–Property Relations

Solution of carbon dioxide in glasses and melts results in increased Qⁿ⁺¹/Qⁿ abundance ratio in the silicate, i.e. the network becomes increasingly polymerized (Eq. (4)). This is the opposite of the effect of dissolved water, which causes the silicate network to depolymerize (Eq. (2)). Therefore, melt and glass properties that vary with melt polymerization will also vary with the concentration of dissolved carbon dioxide. This change will, for example, cause expansion of more polymerized liquidus phases compared with CO₂-free systems. Moreover, configurational heat capacity and entropy would tend to decrease because the partial molar heat capacity of the more polymerized Qⁿ species is smaller than that of depolymerized Qⁿ species. It follows that transport properties will also change with proportion of dissolved carbon dioxide. Experimental data relevant to these important properties are, however, scarce, so many of these predictions cannot as yet be benchmarked against experimental data.

3.3 Reduced Carbon

The reduced carbon species of interest in the C–O–H subsystem of volatiles are CO, C, and hydrocarbons. Among possible hydrocarbons, only CH₄ is found stable under the temperature/pressure conditions of melt precursors of silicate glass.

3.3.1 Solubility, Solution Mechanisms, and Properties

Solubility and solution mechanisms for elemental C in silicate melts and glasses are not well established. By analogy with C solubility in crystalline silicates, it is likely of the order of tens of ppm. This oxidation state, therefore, will not need to be considered further. Likewise, little can be said about carbide solubility and solution mechanisms in silicate–C–O melts, which would obtain in highly reducing, H-free environments but have not been examined to any significant extent.

Carbon monoxide, CO, predominates in the C–O system at the temperatures of molten silicates within comparatively narrow oxygen fugacity range of about 2 log units. The solubility ranges from <100 ppm at ambient pressure and high temperature to 1–2 wt % in the 2–3 GPa range (Figure 6) and is highest at the graphite saturation surface. Experimental data with which to address the effects of silicate composition are not available. From less than a handful of existing experimental studies, however, it appears that the solubility of CO in silicate melts is lower than that of CO₂ at the same pressure, temperature, and silicate compositions. The difference can reach 50 % and decreases with increasingly melt polymerization.

Solution of CO in silicate melts in equilibrium with essentially pure CO gas results in formation of CO₃²⁻-type complexes. However, the exact solution

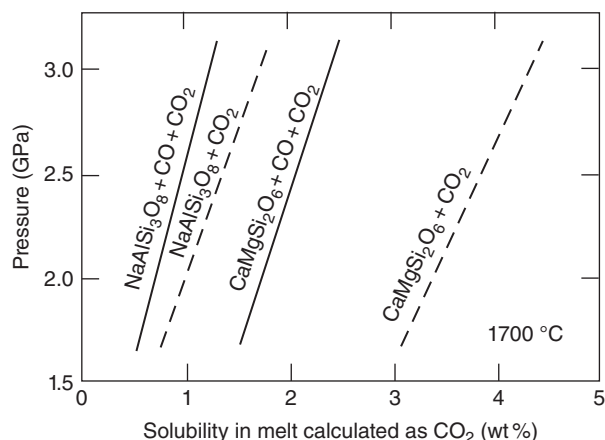
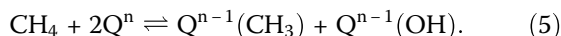


Figure 6 Solubility of CO₂ and CO in melts in equilibrium with either pure CO₂ fluid or mixed CO+CO₂ fluid for the silicate compositions indicated as a function of total pressure at 1700 °C (data compilation by [1]).

mechanism(s) is not clear as this process requires reduction of one or more of the silicate components. This redox couple has not been identified yet.

In silicate–C–O–H systems, methane (CH₄) is the dominant C-bearing gas species under highly reducing conditions. Methane solubility in silicate melts is 60–80% less than that of CO₂ (Figure 7). Methane solution mechanisms, determined by ¹³C MAS NMR and by Raman spectroscopy of glass formed by temperature quenching of melt at high pressure (1–2 GPa), involve methyl groups (CH₃) and molecular CH₄ whose proportions vary with melt composition. An expression to describe the solution mechanism of methane in silicate melts is



In Eq. (5), the Qⁿ species are as described in Chapter 2.2. The notations (CH₃) and (OH) indicate that CH₃ and OH groups form Si–CH₃ bonds in depolymerized Qⁿ⁻¹ species. In principle, this mechanism has many similarities with that described for H₂O (Eq. (2)). It is not surprising, therefore, that dissolved methane affects liquidus phase relations in silicate systems much as does dissolved water. On an equimolar basis, the effect on liquidus temperatures is also about the same as that of water (~10 °C/mol % CH₄ or H₂O).

3.4 Reduced Nitrogen

Nitrogen in silicate melts can be reactive or nonreactive, depending on its oxidation state. Molecular N₂ is stable under oxidizing conditions such as those of air and down to perhaps two to three orders of magnitude lower oxygen fugacity. Because it is nonreactive, it will be described further in Section 4. Under more reducing conditions,

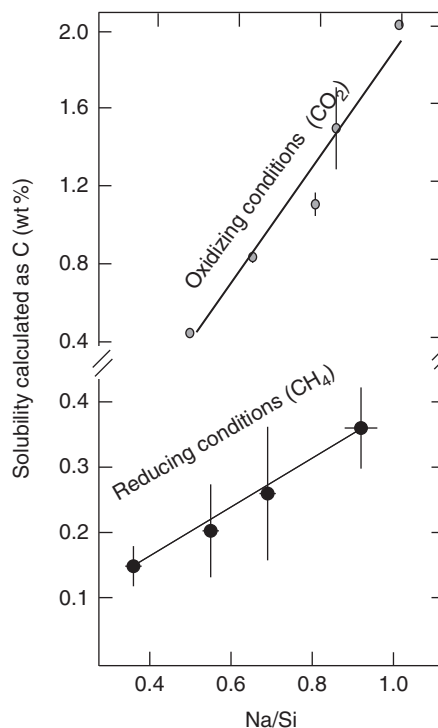
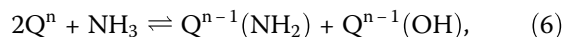


Figure 7 Solubility of oxidized and reduced carbon as a function of Na/Si ratio of Na₂O–SiO₂ melts at 1400 °C and pressures between 1 and 2.5 GPa under either oxidizing or reducing conditions (hydrogen fugacities defined by the 3 Fe₂O₃ + H₂ = 2 Fe₃O₄ + H₂O or FeO + H₂ = Fe + H₂O equilibria, respectively).

nitrogen is more soluble than oxidized nitrogen in silicate–N–O systems. It forms nitride complexes presumably by exchanging with oxygen in silicate tetrahedra, but possibly also with other metal cations, and gives rise to the original oxynitride glass family (see Chapter 7.8). In silicate–N–O–H systems, the nitrogen solubility increases with increasing hydrogen fugacity, *f*_{H₂}, at given temperature and pressure (Figure 8). In such melts, nitrogen and hydrogen react to form ammonia, NH₃, which is nonreactive in silicate melts, and NH₂ groups linked to Si⁴⁺ with resultant breakage of Si–O–Si bridges in the structure



where (NH₂) and (OH) indicate that NH₂ and OH groups bond with Si⁴⁺ in the depolymerized Qⁿ⁻¹ species. In principle, this mechanism resembles that described for H₂O (Eq. (2)) and methane (Eq. (5)). Although little or no experimental data exist with which to characterize the effects of reduced nitrogen on melt and glass properties, we can expect that nitrogen dissolved as NH₂ groups has effects resembling those of dissolved water and methane.

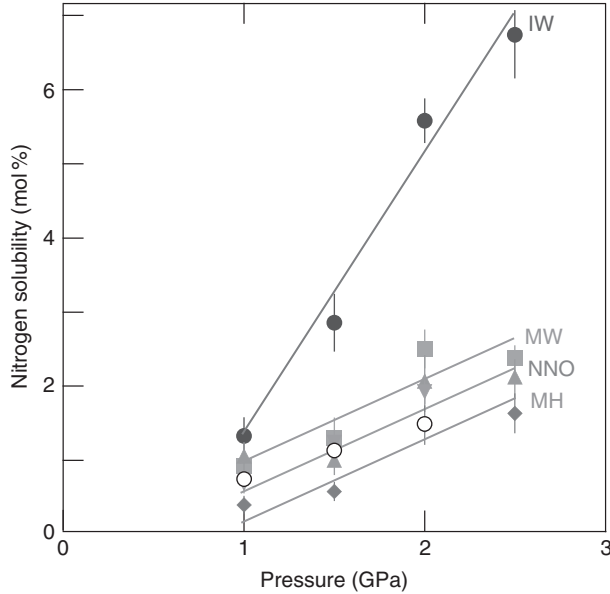
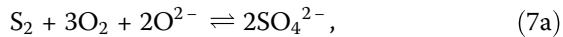


Figure 8 Solubility of nitrogen in quenched $\text{Na}_2\text{Si}_4\text{O}_9$ melt as a function of pressure under the redox conditions indicated. Hydrogen fugacity buffered by the reactions; $3 \text{Fe}_2\text{O}_3 + \text{H}_2 = 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$ (MH), $\text{NiO} + \text{H}_2 = \text{Ni} + \text{H}_2\text{O}$ (NNO), $\text{Fe}_3\text{O}_4 + \text{H}_2 = 3 \text{FeO} + \text{H}_2\text{O}$ (MW), and $\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$ (IW), where the f_{H_2} (IW) $>$ f_{H_2} (MW) $>$ f_{H_2} (NNO) $>$ f_{H_2} (MH) at the same temperature and pressure.

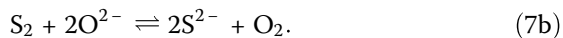
3.5 Sulfur

Sulfur can exist in at least four different oxidation states (S^{6+} , S^{4+} , S^0 , and S^{2-}). Among these, the solubility of elemental sulfur in silicate melts and glasses is likely so small that it will not be considered further. For the other oxidation states, the solubility may reach thousands of ppm while depending on bulk silicate composition, temperature, pressure, and sulfur fugacity, f_{S_2} , and oxygen fugacity, f_{O_2} .

Whether under reducing or oxidizing conditions, sulfur solubility is a positive function of the metal oxide/ SiO_2 ratio of the glass (Figure 9). At constant silicate composition, it first decreases with increasing f_{O_2} and then increases because different solution mechanisms operate for the different redox states. On the oxidizing side of the minimum, one has



where decreasing f_{O_2} results in decreasing sulfur solubility (as SO_4^{2-} groups). On the reducing side of the minimum, the sulfur solubility, now as S^{2-} groups, increases with decreasing f_{O_2} :



These relations can be expanded to describe sulfur speciation with the silicate Q^n species:

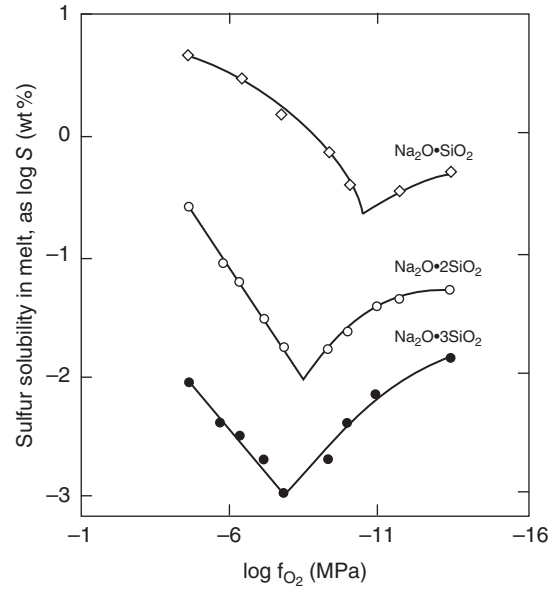
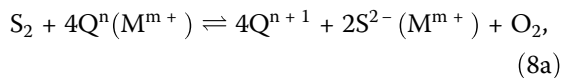
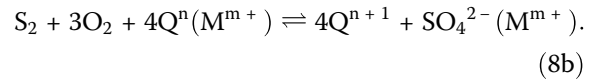


Figure 9 Sulfur solubility in Na_2O - SiO_2 melts as a function of redox conditions in glasses quenched from 1200°C and at ambient pressure (data from [11]).

and



In these expressions, M^{m+} denotes network-modifying cations that also serve to charge compensate the S-bearing functional group.

Expressions (8a) and (8b) illustrate how the redox state of sulfur species is linked to the degree of silicate melt polymerization (here expressed as the abundance ratio, $\text{Q}^{n+1}/\text{Q}^n$). In both cases, decreasing melt polymerization, $\text{Q}^n/\text{Q}^{n+1}$, drives the equilibrium toward the higher solubility, which is as observed.

These same two expressions point to how properties of the M^{m+} cation(s) govern sulfur solubility. This feature is often expressed as sulfur capacity, C_s , which is defined as $C_s = W_{\text{t}_i}(f_{\text{O}_2}/f_{\text{S}_2})$ and embodies the fact the relative stability relations of $\text{Q}^n(\text{M}^{m+})$ and the sulfur species exert strong control on sulfur solubility. This feature has important metallurgical implications that are discussed in Chapter 7.4.

3.6 Halogens

Fluorine and chlorine are the two halogens that have received most attention. Structural and property data are much more extensive for F-bearing than for Cl-bearing glasses and melts in part because fluorine has a quite high solubility even at ambient pressure and because it exerts major effects on glass properties. It is

often assumed that these features are due to the fact that F^- can substitute for O^{2-} in the silicate network in simple systems such as SiO_2-F , having in this sense a role similar to that of OH^- upon water dissolution. For physical properties such as viscosity and liquidus phase relations, however, addition of fluorides to silicate glasses and melts often has substantially different impact on properties compared with that of equimolar proportions of dissolved water.

The solubility of chlorine generally is lower than that of fluorine. Effects of bulk composition on solubility also differ because variations in metal cation type and $Al/(Al+Si)$ ratio, for example, have significantly greater effects on fluorine than on chlorine solubility. Furthermore, the functional relationships between melt composition and solubility differ for the two halogens whose effects on melt and glass properties are quite different. Chlorine barely causes viscosity changes, whereas the effects of fluorine are often of the same magnitude as those of dissolved water. Melting temperatures and melting phase relations are also affected in different ways where, on an equimolar basis, fluorine causes greater freezing point depression than H_2O and is more effective than Cl by several hundred percent.

There are important differences in the solution mechanisms of fluorine in SiO_2 , in metal oxide/ SiO_2 , and in metal oxide/ Al_2O_3/SiO_2 melt and glass systems. The simple SiO_2-F system comprises $Si-F$ bonds, whereas, as determined from ^{19}F MAS NMR data, the dominant solution mechanism in metal oxide/ SiO_2 systems is simple metal fluoride complexing. In aluminosilicate melts, the solution mechanism involves charge-balanced Al^{3+} and Si^{4+} , where the relative import of Si^{4+} and Al^{3+} in the F-bearing complexes correlates with the original Si/Al ratio. In comparison with hydrous metal oxide/ SiO_2 glasses and melts, the metal fluoride complex plays a more important role in the structure than metal oxide- OH complexes [12]. For chlorine, the dominant solution mechanism is interaction between Cl^- and alkali metals or alkaline earths. If there is direct interaction with the rest of the silicate structure, these effects are of subordinate importance.

3.7 Hydrogen

Hydrogen solubility data exist for only a few melt and glass compositions, namely, SiO_2 glass, $NaAlSi_3O_8$ melt, and $CaMgSi_2O_6$ melt. In SiO_2 glass, hydrogen solubility is a linear function of pressure and is comparable to those of the noble gases in silicate melts. These data are consistent with solution of H_2 in molecular form. However, at higher

temperature and pressure, the H_2 solubility is proportional to the square root of pressure, which points to chemical interaction between the dissolved hydrogen and the silicate structure. The freezing point depression of silicate caused by H_2 -rich fluids also suggests that hydrogen interacts chemically with the silicate melt structure [13].

4 Nonreactive Volatiles in Silicate Glass and Melt

The nonreactive volatiles in silicate glasses and melts are the noble gases and molecular N_2 . As already stated, solution of hydrogen, water, carbon dioxide, and methane partly takes place in the form of nonreactive species. In melts and glasses containing several percent or more water, more than 50 % of this water is dissolved in the molecular form H_2O . However, as noted above [Section (3.1)], the proportion of molecular H_2O decreases with increasing temperature above the glass transition. Molecular CO_2 and CH_4 likely also vary with temperature, but few experimental data are available. The proportion of the molecular form is also quite sensitive to bulk composition, so for both the methane and carbon dioxide systems, the more important the molecular and nonreactive forms, the more silica-rich (more polymerized) a melt.

For volatiles that exist exclusively in molecular form in silicate melts and glasses (inert gases and N_2), there is a simple relationship between solubility and atomic or molecular dimensions (Figure 10). Near ambient

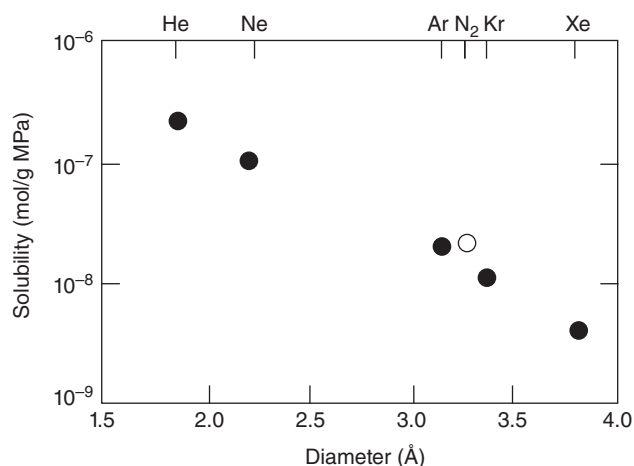


Figure 10 Solubility of nonreactive gases in tholeiite basalt melts at ambient pressure and 1350 °C as a function of atomic/molecular diameter (data from [14, 15]).

pressure, the noble gas solubility, X_i , is proportional to its concentration in the gas phase, P_i , via a proportionality constant, K_i :

$$X_i = K_i P_i. \quad (9)$$

So the K_i value (Henry's law constant) for a given silicate composition is negatively correlated with the atomic radius of the noble gas. This constant increases with silica content of the melt.

The temperature dependence of noble gas solubility is slight and can be either positive or negative, whereas the K_i value decreases nonlinearly with pressure. The deviation from linearity increases with pressure and with noble gas atomic radius. In natural silicate melts, the enthalpy of solution, ΔH_s , ranges from near 5 to about 20 kJ/mol and decreases with increasing atomic radius. This enthalpy becomes increasingly sensitive to melt polymerization (equivalent to metal/silicon ratio) as the atomic radius of the noble gas increases.

The solubility mechanism or mechanisms of noble gases in silicate melts and glasses have been modeled with the assumption that the gas occupies holes in the structure. For example, the partial molar volumes obtained from solubility measurements estimate the porosity of SiO_2 glass. The partial molar volumes in silica glass are 16.4 ± 1.4 , 10.3 ± 2.3 , and $5.5\text{--}10.8 \text{ cm}^3/\text{mol}$ for Ar, Ne, and He, respectively.

5 Perspectives

Many volatile components commonly dissolve in the form of simple anionic complexes (e.g. OH groups, CO_3 groups, etc.). To develop an understanding of how volatiles affect structure and properties of glasses and melts, however, it is necessary to establish how these reactive functional groups interact with the silicate structure. This goal may now be attainable with the aid of modern spectroscopic methods. Ideally, such characterization should be conducted while the samples are at the temperatures and pressures of interest because temperature quenching and decompression of a melt can lead to changes in both concentration of the volatile component(s) and their structural interaction. Numerical simulations of solution mechanisms also show promise and likely will become more important in the future as computational capacities and speed advance. For nonreactive solution, such approaches will, for instance, picture how "inert" gases contribute themselves to the formation of the cavities in which they are accommodated. Integrated

examination that combines simulation with *in situ* experiments will add further to the development. Technology has slowly becoming available with which at least structural characterization at high temperature and pressure can be carried out. Solubility data may also be obtained in this manner, provided that the temperature and pressure effects necessary to translate instrumental information into solubility are known. For example, infrared absorption can be conducted with melts, but temperature and pressure effects on molar absorption coefficients are poorly known. The principles are beginning to emerge and will give a sounder basis to thermodynamic modeling of volatile–melt equilibria (Chapter 5.3).

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5.6

Redox Thermodynamics and Kinetics in Silicate Melts and Glasses

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1 Introduction

Size and charge are first-order considerations of the cation role in the structure of ionic melts and glasses. But many cations, particularly of transition metals, are heterovalent, that is, the cation charge and size are affected by the chemical potential of the oxidizing elements. Consequently, redox potential becomes not only (i) a tool in engineering the properties of synthetic melts and glasses but also (ii) a variable in the service properties of formed glasses, both synthetic and natural.

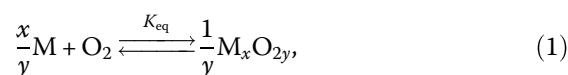
The thermodynamics involved in the study of redox are reasonably straightforward, the caveat being the standard one for multicomponent solutions, i.e. the need to know the relationship between component activity and component concentration. Redox dynamics, i.e. the coupling of thermodynamics with kinetics, are more complicated. Here, dynamics are considered from two end-member perspectives: *closed systems*, where the redox potentials of various component cations interact on a short time-scale such that reactions are local (nominally at atomic scale), and *open systems*, in which the structural state of the melt or glass is being modified dynamically by an external redox potential. The establishment and control of color in glass or the use of redox reactions in glassmelt fining are examples of the former, while the float-glass process and the ambient-environment “weathering” of synthetic and natural glasses are examples of the latter. The heterovalency of ions (both of cations and some anions, e.g. those of sulfur) effects semiconductor properties in the melts/glasses, which is important in both closed- and open-system contexts.

In what follows, redox thermodynamics are considered from the perspective of the chemical potentials/activities of oxides and not of ions. As learned from Hermann Schmalzried [1], this is distinctly practical: one can control straightforwardly the activities of oxides (and of other neutral elements or compounds) in experimental and production settings; the same is not true for the activities of ions. Nevertheless, one can consider redox based on an ion-activity perspective (e.g. Chapter 5.9). Additionally, for simplicity, this chapter emphasizes silicate glassmelts and glasses. The extrapolation of the ideas and approach presented here to SiO₂-free oxide and halide melts and glasses is straightforward. The challenge is almost always in having good, useful solution models for these complex multicomponent systems.

2 Oxidation/Reduction Thermodynamics

2.1 Reference Reactions: Pure Metal to Pure Metal Oxide; Pure Oxide to Pure Oxide of Different Valence

The relative oxidation potentials of the various elements are the natural starting point for treating redox reactions in multicomponent melts and glasses. One can discern them by examining the reference reactions in which a pure metal reacts with pure molecular oxygen. Because we are interested in relative potentials, the reactions should each be written in terms of one mole of O_{2(g)}, i.e.



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where, applying the law of mass action, one expresses the equilibrium constant K_{eq} as

$$K_{\text{eq}} = \frac{[a_{\text{M}_x\text{O}_y}]^{1/y}}{[a_{\text{M}}]^{x/y}[a_{\text{O}_2}]} = \exp\left(\frac{-\Delta_r G_{(1)}^\circ}{RT}\right). \quad (2)$$

In Eq. (2), a_i is the activity of species i , RT has the usual meaning, and $\Delta_r G_{(1)}^\circ$ is the standard Gibbs free energy of reaction (1), “standard” because reaction (1) involves “pure” reactants creating “pure” products, i.e. no solutions are involved. At equilibrium, the metal M and the metal oxide are both present: $a_{\text{M}} = a_{\text{M}_x\text{O}_y} = 1$; consequently, Eq. (2) can be rewritten as

$$\Delta_r G_{(1)}^\circ(T) = -RT \ln K_{\text{eq}} = RT \ln a_{\text{O}_2}. \quad (3)$$

At low pressures, the activity of oxygen is equivalent to the partial pressure, p_{O_2} (in atmospheres). As stated by the Gibbs phase rule, for a pure metal–pure metal oxide in equilibrium, two phases coexist in a two-component system, so Eq. (3) is directly employed to define the metal–metal oxide buffer for oxygen.¹ At elevated pressures the formalism remains the same, but one must use instead G.N. Lewis’ fugacity function, i.e. $\Delta_r G_{(1)}^\circ(T) = RT \ln f_{\text{O}_2}$, if the relationship between fugacity and activity is known.

In Eqs. (2)–(3), $\Delta_r G_{(1)}^\circ$ has enthalpic and entropic components, i.e. $\Delta_r G_{(1)}^\circ = \Delta_r H_{(1)}^\circ - T\Delta_r S_{(1)}^\circ$, where H and S of each reactant and of the product in reaction (1) are both functions of temperature: at any specified T , then, $\Delta_r H_{(1)}^\circ$ and $\Delta_r S_{(1)}^\circ$ can be calculated via integration of $\Delta_r C_p(T)$ and $\Delta_r C_p(T)/T$, respectively, where C_p is the isobaric heat capacity, which is, in general, a nonlinear function of T . To the $\Delta_r G_{(1)}^\circ(T)$ so calculated, a function can then be adjusted, typically of the form $\Delta_r G_{(1)}^\circ(T) = A + BT \log T + CT$, where A , B , and C are constant fit parameters. Tables of such data for standard oxidation reactions are readily available in the literature (e.g. [2, 3]).

A graph of $\Delta_r G_{(1)}^\circ(T)$ [$= RT \ln a_{\text{O}_2} = RT \ln (p_{\text{O}_2}, \text{atm})$] vs. T is presented as Figure 1 (after [4] and the references therein). This type of plot is known as an Ellingham

diagram; the additional axis for the oxygen activity (partial pressure in atm) is explained below.² Because the reactions follow the form of reaction (1), i.e. each in terms of 1 mol of $\text{O}_{2(\text{g})}$ reactant, the relative oxidation potentials of metals and of transition metal oxides are revealed, with more negative values of $\Delta_r G_{(1)}^\circ$ representing a greater oxidation potential (i.e. a more stable oxide). Immediately obvious is that the data for each reaction plot essentially as a straight line (or a continuous series of straight lines with slope changes corresponding to phase changes of the reactants and/or products): the temperature sensitivity of $\Delta_r G^\circ$ is the blatant one associated with the relationship $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, that is, the temperature sensitivities of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are revealed as second-order effects. As such, the slopes of the solid metal-to-solid metal oxide “curves,” for example, indicate that the entropy decrease associated with incorporation of a mole of O_2 gas into a crystalline solid is approximately -185 J/mol/K . In passing, note that a reaction in which 1 mol of $\text{O}_{2(\text{g})}$ reacts with a solid to produce 1 mol of a gaseous oxide, e.g. $\text{C} + \text{O}_{2(\text{g})} = \text{CO}_{2(\text{g})}$, has approximately a zero slope, whereas one in which 2 mol of product gas are formed, e.g. $2 \text{C} + \text{O}_{2(\text{g})} = 2 \text{CO}_{(\text{g})}$, has a negative slope. The highest values on this Ellingham diagram correspond to elements such as Cu, Fe, Ni, Co, and also Au, Ag, and the platinum-group elements considered by geochemists to be *siderophile* (literally, iron loving); the lowest values are, in contrast, for elements such as Ca, Al, Li, Ti, and Si that are considered as *lithophile* (rock loving).

One ramification of plotting $RT \ln (p_{\text{O}_2}, \text{atm})$ vs. T is that any straight line that goes through the origin of the graph, $\Delta_r G_{(1)}^\circ = 0$ and $T = 0 \text{ K}$ (the point labeled as O in the upper left-hand corner of the diagram), has a slope of $R \ln p_{\text{O}_2}$, i.e. it is a line of constant oxygen activity: this is the foundation of the farthest-out external scale (along the graph’s right-hand side and bottom) labeled p_{O_2} . The straightforward way to use the graph is to evaluate the slope of a line emanating from the origin through the point where a specific $\Delta_r G_{(1)}^\circ$ reaction curve intersects a specified temperature. For example, to determine at 1400°C the oxygen activity at which nickel and nickelous oxide are in equilibrium, the so-called Ni : NiO (“NNO”) buffer for oxygen, one extends a line from the point O through the point $\Delta_r G_{(\text{Ni:NiO}; 1400^\circ \text{C})}^\circ$ and reads the appropriate p_{O_2} off the far-right axis: at this temperature, NNO is $p_{\text{O}_2} \cong 2 \times 10^{-6} \text{ atm}$ ($a_{\text{O}_2} \cong 2 \times 10^{-6}$).

¹ K_{eq} is defined for isobaric conditions; hence pressure is ignored in Eqs. (2) and (3). $\Delta_r G_{(1)}^\circ$, of course, is a function of both temperature and pressure, but as Gibbs free energy is a state variable, it can be evaluated along any arbitrary path. This presentation, thus, will concentrate on (isobaric) temperature sensitivity; the analysis is extrapolated to other pressures nominally straightforwardly through evaluation of the pressure effects on enthalpy and entropy. The “nominal” caveat is related to the requirement of having good data and models for the equations of state of the phases involved.

² There are also axes corresponding to gas mixing ratios for $\text{H}_2:\text{H}_2\text{O}$ and for $\text{CO}:\text{CO}_2$, which can be used to design a controlled-oxygen-activity atmosphere – via gas-phase reaction/equilibrium – at a specified temperature; see Ref. [4].

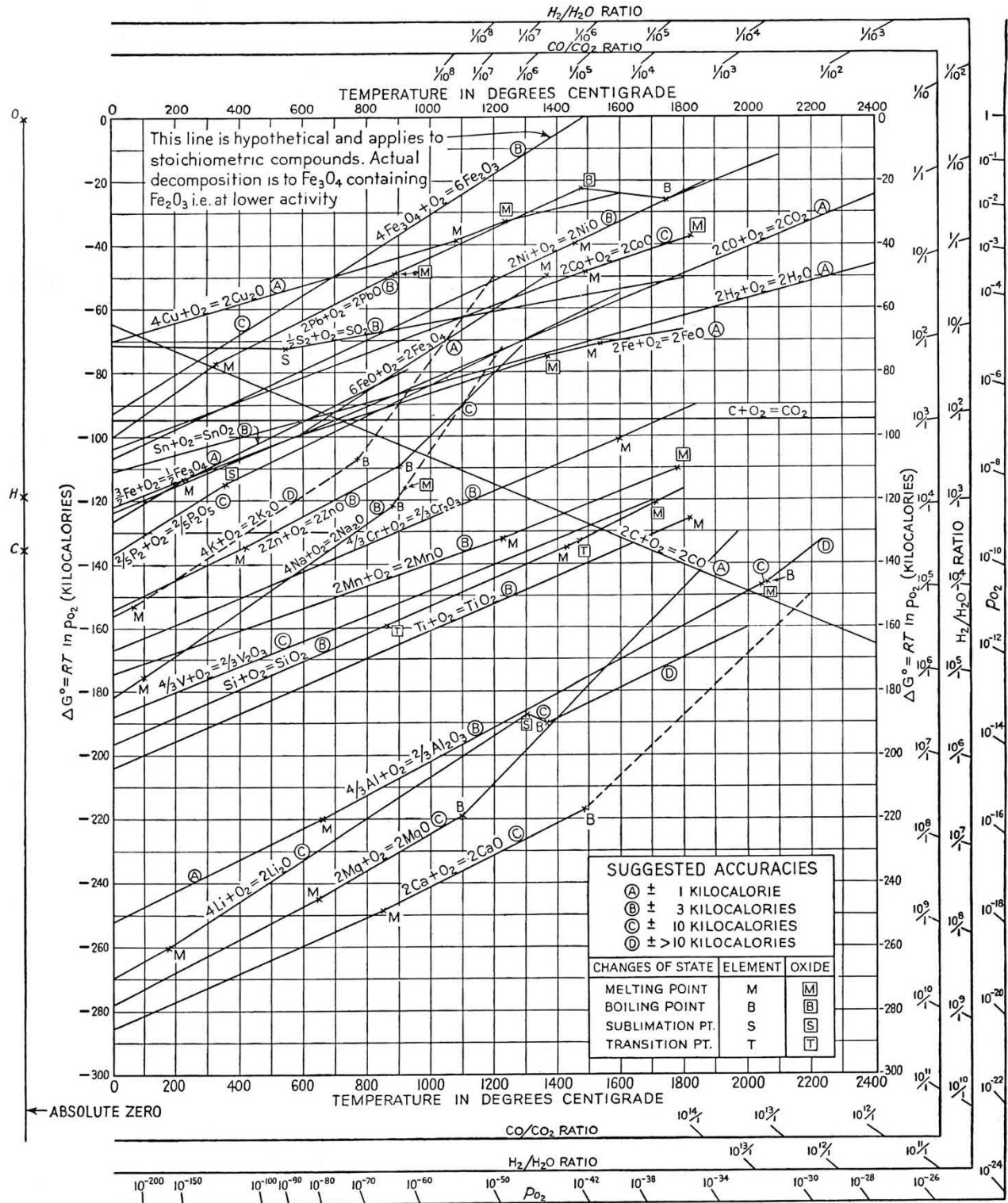
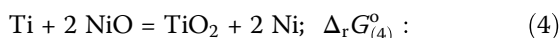


Figure 1 Ellingham diagram as modified by Richardson and Jeffes [4]: $\Delta_r G^\circ (=RT \ln p_{\text{O}_2})$ vs. T at ambient pressure. All reference reactions are written in terms of 1 mol of oxygen; thus plotted, the relative oxidation potentials of metals and of transition metal oxides are revealed, with more negative values of $\Delta_r G^\circ$ representing a greater oxidation potential (i.e. a more stable oxide) (1 kcal = 4.184 kJ).

Another use of the Ellingham plot is determinations of phase equilibria. Consider, for example, two specimens, one of pure Ni and the other of pure Ti, both placed in a closed system along with some pure oxygen gas, but not enough to convert fully the Ti to TiO_2 or the Ni to NiO. After a long reaction time, one predicts that the thermodynamically stable state would be a rind of TiO_2 on the Ti specimen and unoxidized Ni, with the oxygen activity of the system lowered to the Ti : TiO_2 buffer. But this experiment only “works” if the two metal specimens are not touching and if the temperature is low enough that the vapor pressures for Ti and Ni are minimal. In other words, pure Ti has a significantly greater oxidation potential than pure Ni.

This analysis is consistent with describing the reference Ti–Ni–O *displacement reaction*:



where oxygen is “displaced” from bonding with Ni to bonding with Ti. In Eq. (4) $\Delta_r G_{(4)}^\circ$ is a function of T ; it can be determined directly on the Ellingham diagram: at a fixed temperature, $\Delta_r G_{(4)}^\circ$ is the (vertical) distance between the Ni : NiO and Ti : TiO_2 buffer lines (e.g. at 1400°C , $\Delta_r G_{(\text{Ti}:\text{TiO}_2)}^\circ \approx -600 \text{ kJ}/[\text{mol O}_2]$ and $\Delta_r G_{(\text{Ni}:\text{NiO})}^\circ \approx -180 \text{ kJ}/[\text{mol O}_2]$; thus, $\Delta_r G_{(4)}^\circ \approx -420 \text{ kJ}/[\text{mol O}_2]$). It is significant to note that the Ni : NiO and Ti : TiO_2 buffer lines do not cross: consistent with the Gibbs phase rule, there is no oxygen activity at which phase-pure Ti, TiO_2 , Ni, and NiO are simultaneously stable at any given temperature. Further, it would be incorrect to interpret the Ellingham diagram or reaction (4) as suggesting that rutile ($\alpha\text{-TiO}_2$) precipitating in a Ni matrix is a thermodynamically stable assemblage: in such a hypothetical system, neither a_{NiO} or a_{Ti} is unity, which is the prerequisite for such a simple interpretation.

The Ellingham diagram (Figure 1) includes, too, reactions for heterovalent cation oxides, specifically $6 \text{FeO} + \text{O}_{2(g)} = 2 \text{Fe}_3\text{O}_4$ (the wüstite–magnetite [WM] buffer) and $4 \text{Fe}_3\text{O}_4 + \text{O}_{2(g)} = 6 \text{Fe}_2\text{O}_3$ (the magnetite–hematite [MH] buffer); other versions of the diagram might include similar reactions, e.g. for the various valence oxides of Mn (critical for dry cell battery chemistry) or Sn (critical for the float-glass process, as seen below). As evidenced by the line-like topology of their respective $\Delta_r G^\circ$ curves, the thermodynamics of these oxide–oxide reactions is identical to that of the metal–metal oxide reactions.

2.2 General Redox Reactions: The Case of Solutions

The comment concerning the non-stability of an Ni– TiO_2 composite and the parenthetical caveat about the Ni–Ti– $\text{O}_{2(g)}$ thought experiment, both presented above,

are an admonition: care must be exercised in applying the Ellingham diagram to redox problems when one is considering solutions, e.g. oxidation of metal alloys and/or redox conditions in multicomponent oxides like glasses or glassmelts. As the activities of either products or reactants shift away from unity, the Gibbs free energy driving potential is changed. This is accounted for through use of the activity quotient:

$$\Delta_r G_{(1)}(T) = \Delta_r G_{(1)}^\circ(T) + RT \ln \left(\frac{\prod_i a_i^{n_i} \text{ products}}{\prod_i a_i^{n_i} \text{ reactants}} \right), \quad (5)$$

where $\prod_i a_i^{n_i}$ are the products of the relevant activities, each raised to its respective stoichiometric coefficient (n_i). The correction term in Eq. (5) is a linear function of temperature and additionally is equal to zero at $T = 0 \text{ K}$. Given that $\Delta_r G_{(1)}^\circ(T)$ is effectively a straight line, one recognizes that, on the Ellingham diagram, the activity-quotient term simply rotates the standard-reaction free energy function about its intercept on the ordinate (i.e. about $\Delta_r H_{(1)}^\circ$ at 0 K). As different metal–metal oxide buffer lines rotate because of the activity effect, one discovers redox couples that are “unexpected,” i.e. electron exchanges reducing what are considered more stable oxides and oxidizing what are considered more noble metals.

A useful example is the redox reaction occurring in the float process for soda-lime-silica flat glass (“NCS,” which includes small amounts of Al_2O_3 and/or MgO). The original invention by Pilkington, Ltd., seemed straightforward enough: float glassmelt as a continuous ribbon on a bath of liquid metal ([5], Chapter 1.4). The metal for the float bath had six technical prerequisites: (i) an appropriate temperature range of liquid stability ($T_m < 600^\circ\text{C}$; $T_b > 1050^\circ\text{C}$), (ii) a low vapor pressure at the high- T condition ($p_i \sim 10^{-7} \text{ atm}$ at 1050°C), (iii) a density much exceeding that of NCS ($\rho_{\text{NCS};1050^\circ\text{C}} \sim 2.5 \text{ g/cm}^3$), (iv) distinct nobility relative to the metals composing the oxides of the NCS glassmelt (i.e. a siderophile element), (v) ease of environmental oxidation control, and (vi) low toxicity. Molten tin was the obvious choice, particularly when economic considerations were added to the technical ones. The process development was challenging because of the reaction between the liquid NCS and the liquid Sn. Pilkington [5] did not consider the reaction problem from the perspective of redox thermodynamics, but the redox understanding is actually crucial [6].

At its original contact with the liquid-Sn bath at $T \approx 1050^\circ\text{C}$, the NCS glassmelt contains very little – to first order, none – of the tin oxides SnO and SnO_2 ; similarly, the high-purity Sn float bath contains very little Na, Ca, or Si metal. But consider the reaction of Sn to stannous oxide in the context of the float reaction,

i.e. $2 \text{Sn}_{(l)} + \text{O}_{2(g)} = 2 \text{SnO}_{(l)}$. Not shown in Figure 1, the reference-reaction $\Delta_r G_{(\text{Sn}:\text{SnO})}^\circ(T)$ line is very close to the one for $\text{Fe}:\text{FeO}$ (Figure 2). Application of Eq. (5) gives

$$\Delta_r G_{(\text{Sn}:\text{SnO})}(T) = \Delta_r G_{(\text{Sn}:\text{SnO})}^\circ(T) + RT \ln \left(\frac{a_{\text{SnO}}^2}{a_{\text{Sn}}^2 p_{\text{O}_2}} \right). \quad (6)$$

At the glassmelt/liquid-Sn interface, at the initial contact of the glassmelt with the float medium, $a_{\text{Sn}} \cong 1$ and p_{O_2} is set by the forming-gas ($\text{H}_2:\text{N}_2$) atmosphere that is sustained in the float-bath chamber ($\sim 10^{-14}$ atm at 1050°C ; this is also the activity of oxygen in the liquid tin). As noted above, however, a_{SnO} in the glassmelt is essentially zero. As a consequence, the activity-quotient term in Eq. (6) is negative, and strongly so, $\Delta_r G_{(\text{Sn}:\text{SnO})}(T)$ is a line strongly rotated clockwise from that characterizing $\Delta_r G_{(\text{Sn}:\text{SnO})}^\circ(T)$ (Figure 2). Continuing, one can consider the $\text{Na}:\text{Na}_2\text{O}$ equilibrium for the float situation ($4 \text{Na}_{(l)} + \text{O}_{2(g)} = 2 \text{Na}_2\text{O}_{(l)}$):

$$\Delta_r G_{(\text{Na}:\text{Na}_2\text{O})}(T) = \Delta_r G_{(\text{Na}:\text{Na}_2\text{O})}^\circ(T) + RT \ln \left(\frac{a_{\text{Na}_2\text{O}}^2}{a_{\text{Na}}^4 p_{\text{O}_2}} \right). \quad (7)$$

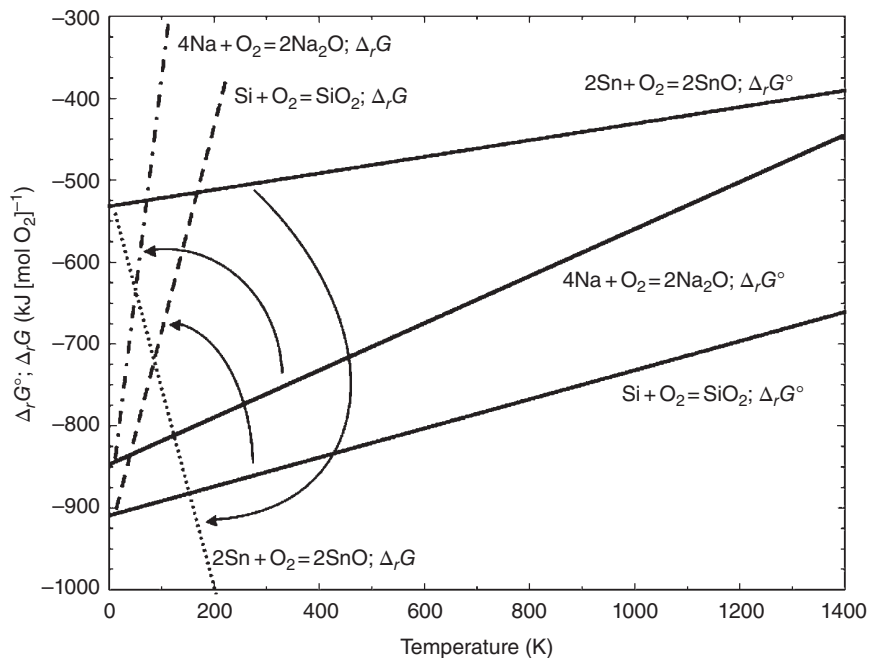
At the glassmelt/liquid-Sn interface, $a_{\text{Na}_2\text{O}}$ is initially that of the glassmelt ($\sim 10^{-1}$), p_{O_2} is again that of the forming-gas atmosphere, but a_{Na} in the liquid Sn is vanishingly small. As a consequence, $\Delta_r G_{(\text{Na}:\text{Na}_2\text{O})}(T)$ is a line strongly rotated counterclockwise from the reference

$\Delta_r G_{(\text{Na}:\text{Na}_2\text{O})}^\circ(T)$. A similar analysis can be done for $\text{Si}:\text{SiO}_2$: $a_{\text{Si}} \rightarrow 0$ in the liquid Sn, and so the reference-reaction curve rotates counterclockwise. As illustrated in Figure 2, the $\Delta_r G_{(i)}(T)$ lines thus cross: the result is a large driving potential for Sn from the float bath to be oxidized (and added to the glassmelt ribbon) in a coupled reaction with SiO_2 and Na_2O from the glassmelt, which are reduced (and added to the liquid-metal float bath). The magnitude of the $\Delta_r G$ driving potentials for these redox couples is that of an isothermal vector from the $\Delta_r G_{(\text{Sn}:\text{SnO})}(T)$ line to either of the $\Delta_r G_{(\text{Na}:\text{Na}_2\text{O})}(T)$ or $\Delta_r G_{(\text{Si}:\text{SiO}_2)}(T)$ lines.

The activity effect illustrated in Figure 2 is important to understand, too, for any metal crucible-glassmelt reaction, including the incorporation of ionic platinum into a glassmelt through a redox couple of Pt with silica ($\pm$ less stable oxide components of the glassmelt) (e.g. [7]). The kinetics of such a reaction will be discussed below, including its implications for the chemical morphology and performance of float-processed flat glass.

A clear ramification of the thermodynamics presented here is that design of any melting and delivery process in glass manufacturing strongly depends on understanding the activity-composition relationships both in glassmelts and in the metal or ceramic materials with which they come in contact. Unfortunately, this is not straightforward: silicate melts are distinctly complex solutions (Chapter 5.3); metallic melts can be similarly complex, particularly those involving alloying with the group 14 metalloid elements, which include Sn and Si and are prominent in the float process. Silicate melt solutions

Figure 2 Ellingham diagram (after [6]) for several oxides in the float-glass reaction, for reference conditions ($\Delta_r G^\circ$; solid lines), and for the (non-reference) conditions characteristic of the liquid-Sn/glassmelt interface ($\Delta_r G$; broken lines). The curved arrows indicate the direction of rotation of the $\Delta_r G^\circ$ lines according to Eqs. (5)–(7). Because of the thermodynamics of solution formation, there is an extremely large driving potential for the reduction of components in the glassmelt (e.g. Na^+ and Si^{4+}) and the related oxidation of the liquid-Sn float medium.



are often described via polymerization (e.g. [8]) or quasi-chemical models (e.g. [9], Chapter 5.3). The latter consider silicate melts as solutions of discrete, distinctly ordered multi-ion units and are the basis for automated calculation of relatively simple systems with two or three oxide components, as, for instance, made by the calculator FactSageTM (Facility for the Analysis of Chemical Thermodynamics, Center for Research in Computational Thermodynamics, École Polytechnique de Montréal, Canada, and GTT-Technologies, Herzogenrath, Germany; <http://www.factsage.com>.) Intriguingly, complex multicomponent natural silicate melts are well modeled as regular solutions (i.e. with an ideal entropy of solution and usually a nonzero enthalpy of solution) if the appropriate units are selected as components, e.g. Fe_2SiO_4 and Mg_2SiO_4 entities instead of FeO and MgO , CaSiO_3 instead of CaO , etc. This is the approach of the quasi-chemical thermodynamic calculator MELTS and its derivatives ([10], OFM Research, Inc., Seattle, WA, USA; <http://melts.ofm-research.org/index.html>).

3 Oxidation/Reduction Kinetics

The kinetics of redox reactions in silicate melts and glasses is complicated by two physical factors. (i) The “equilibrium” structure of a glass or glassmelt depends on the valence states of the component ions (e.g. [11], Chapter 2.4); as such, redox reactions are accompanied by structural relaxations that have a direct effect on ion mobility. (ii) For transition metal cations, particularly, but also ionized metalloids such as S and Si, the incorporation of heterovalent ions affects the electronic transference number such that, for a broad range of temperatures, the electrical conductivity of a glass or glassmelt, although decidedly modest (Chapter 4.2), is effected almost exclusively by electronic species, namely, electrons in the conduction band and/or electron holes in the valence band. In condensed matter kinetics, this feature is described as the “semiconductor condition” (e.g. [1], p. 81): for electronic species, the product of concentration and mobility, that is, the transport coefficient, outstrips that of any of the ions; the result is that the fluxes of ions are all decoupled, one from another. The combination of the two effects allows for curious, sometimes surprising reaction morphologies or textures.

When a system is subjected to a differential in thermodynamic potentials that moves it out of equilibrium, the only “rule” in kinetics is that it must evolve in a manner that lowers its Gibbs free energy. There is no requirement that the system achieves a new stable equilibrium; metastable states are possible – and likely – as are discrete transient morphologies for systems continuing to evolve

as a differential potential persists. Applied to the ionic systems considered here, an additional caveat is that near-atomic-scale charge neutrality must be preserved. The situation would be more complex if glass-ceramic materials were considered because the metastability of the crystalline phase(s) would require an additional constraint on ionic flux.

The kinetics of redox reactions will be considered from two end-member perspectives.

(i) *Open systems* are where a glass or glassmelt reacts with the external environment in the process of reaching equilibrium with it through far-beyond-atomic-scale electrochemical diffusion; these situations cover both manufacturing (e.g. in the float-glass process, the continuing reaction between the liquid-metal float bath and the glassmelt ribbon) and application (e.g. oxidation of glasses originally manufactured in reducing situations but subjected to persistent use at ambient conditions characterized by a high chemical potential of oxygen).

(ii) *Closed systems* are where redox potentials are created within the glassmelt solely by the quenching process. The reactions are then local: electronic transfer associated with redox and the related structural relaxation occurs at the near-atomic scale. Closed-system understanding is important in the control of color, is put to use in glassmelt fining, and addresses manufacturing problems caused by glassmelt–crucible reactions.

4 Open-System Redox Dynamics

Consider an FeO-bearing aluminosilicate melt subjected to an environment in which the majority of Fe^{2+} is not stable. This situation happens frequently in nature with basaltic magma, an aluminosilicate melt whose nine main oxide components include the transition metal oxides FeO , MnO , and TiO_2 . In the partially molten upper mantle of Earth, redox equilibrium is originally achieved at conditions that can be taken as $T \sim 1250^\circ\text{C}$ and $p_{\text{O}_2} \approx 10^{-8}$ atm, giving a $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ of ~ 0.1 . Upon eruption, the basalt is very quickly brought to ambient conditions with a $p_{\text{O}_2} = 0.21$ atm that of course persists; consequently, the basaltic glass formed in the eruption oxidizes with time, i.e. with continued exposure to the ambient environment. Ignoring convection, this oxidation must proceed by chemical diffusion, but the issue then is to determine which species are migrating.

4.1 The Phenomenology of Open-System Oxidation

The open-system oxidation problem, specifically where the valence of iron and its impact on structure of the glass

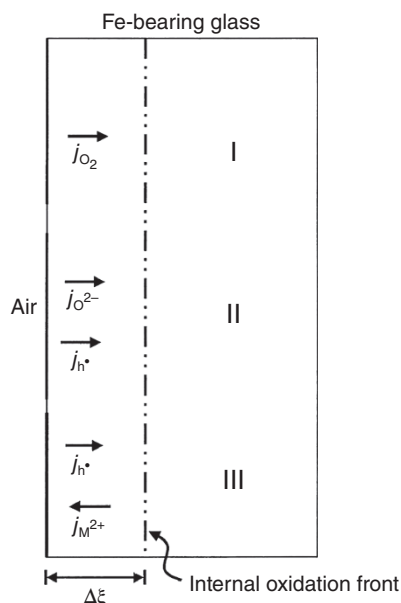


Figure 3 Kinetic modes for the oxidation of a Fe^{2+} -rich aluminosilicate glass or melt, drawn as having the external environment being that of air ($p_{\text{O}_2} = 0.21 \text{ atm}$) [12]. Three independent “modes” – I, II, and III – are illustrated.

or melt are the redox response, is presented phenomenologically in Figure 3 [12]. Three distinct dynamic responses – “modes” – to the oxidation potential are distinguished: one involving the chemical-diffusion flux of molecular O_2 (j_{O_2} ; mode I) and two others involving ionic diffusion, mode II for anion diffusion/flux, $j_{\text{O}^{2-}}$, and mode III for cation diffusion/flux, $j_{\text{M}^{2+}}$. The three modes occur simultaneously at mutually independent rates: the mode that dominates the redox kinetics is the one with the fastest initial response, i.e. that allows the internal reaction front to migrate from the free surface most rapidly. The dominant mode does not necessarily lead to the lowest Gibbs free energy state for the glass or glassmelt. This feature moves the drawing a bit away from simple phenomenology: Fe^{2+} has its primary role in a silicate glass or glassmelt as a network modifier; as the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio increases with oxidation, Fe^{3+} more and more fills a network-former role ([11], p. 351). The internal reaction front, then, is that location where the oxygen activity becomes sufficiently high that the structural change occurs. With the molecular change, the mobility of atoms and of ions changes also.

For broad ranges of temperature and iron content (temperature as low as 800°C with a total $\text{Fe}^{2+} + \text{Fe}^{3+}$ content $\sim 10^{-2}$ at %), mode III dominates the oxidation dynamics of aluminosilicate melts and glasses [12]. Divalent network-modifying cations stream to the free surface where they react with environmental oxygen to produce (with sufficient concentration and thermal energy and/or

time) crystalline thin films of SiO_2 -free, single-cation oxides or multiple-cation oxide solid solutions or compounds such as spinel. The outward flux of cations is charge-compensated by a counterflux of electron holes, j_{h^*} . As for h^* , it is an electronic defect having a single positive charge, which is denoted by the superscript dot; the creation of the electron holes near the free surface is the source of the electrons necessary for the ionization of oxygen that is required to form the crystalline surface oxides.³ The glass or glassmelt is oxidized internally, at the internal reaction front *not* by the addition of oxygen but rather by the removal of cations, i.e. the O^{2-} -to-cation ratio does increase, but by the removal of cations. The kinetics overall are rate limited by the diffusion of divalent network-modifying cations: the distance to the redox front from the free surface, $\Delta\xi$, follows parabolic kinetics, i.e.

$$(\Delta\xi)^2 = 2k'_p t; \quad k'_p \propto X_{\text{M}^{2+}} \bar{D}_{\text{M}^{2+}} \frac{\Delta_r G}{RT}, \quad (8)$$

where k'_p is the parabolic reaction-rate constant, $X_{\text{M}^{2+}}$ is the mole fraction (concentration) of the mobile divalent network-modifying cations in the region between the free surface and the internal oxidation front (i.e. across $\Delta\xi$), and $\bar{D}_{\text{M}^{2+}}$ is the average diffusion coefficient for the divalent cations in the oxidized region (cf. [1], p. 172). As emphasized by Eq. (8), the kinetics of a diffusion-rate-limited reaction is a product of (i) the mobile-species concentration with (ii) the species mobility and with (iii) the normalized (to RT) driving potential of the reaction. An average diffusion coefficient is cited because the mobility of an ion should generally be affected by the oxygen activity (see below), which, of course, varies across thickness $\Delta\xi$.

Mode III oxidation dynamics in aluminosilicate glasses and glassmelts have a direct parallel in the dynamics of oxidation of crystalline oxides and silicates. In the crystalline state, decoupled cation fluxes occur against an immobile O^{2-} sublattice since the transport coefficient for oxygen anions is orders of magnitude smaller than that of many of the cation species, Si^{4+} being one of the obvious exceptions ([1], p. 171). Oxidation of glasses and glassmelts suggests that cation diffusion, specifically that of network-modifying cations, occurs against the relative immobility of the ionic species involved in the network.

³ Mode III kinetic response is *prima facie* evidence that the semiconductor condition holds for iron-oxide-bearing glasses and glassmelts. FeO-bearing, multicomponent crystalline oxides/silicates or glassmelts/glasses are broadly demonstrated to be *p*-type (i.e. h^* ; the *p* stands for positive) semiconductors: over a broad range of temperature and of FeO composition, the conductivity of the material occurs via electron transfer from Fe^{2+} to Fe^{3+} within the valence band of the material, that is, charge transfer occurs by the motion of vacant electron states (“holes”) within the otherwise filled valence band.

Because the dynamics in the crystalline state are effected by the motions of point defects, the similar dynamics in glassmelts and glasses suggests a parallel to point defects that are operative in the amorphous state. As consequence, one can couple a phenomenological description of the kinetics with a qualitative understanding of the dynamics that identifies defects and their reaction-impelled motion in the amorphous state.

Kinetically, phenomenologically, mode III can be understood by evaluating the two active compensating fluxes, $j_{M^{2+}}$ and $j_{h^{\cdot}}$, using Fick's first law, i.e.

$$\begin{aligned} j_{M^{2+}} &= \frac{-c_{M^{2+}} D_{M^{2+}}}{RT} \frac{d\eta_{M^{2+}}}{d\xi} \\ &= \frac{-c_{M^{2+}} D_{M^{2+}}}{RT} \left(\frac{d\mu_{M^{2+}}}{d\xi} + 2F \frac{d\varphi}{d\xi} \right) \end{aligned} \quad (9)$$

and

$$j_{h^{\cdot}} = \frac{-c_{h^{\cdot}} D_{h^{\cdot}}}{RT} \frac{d\eta_{h^{\cdot}}}{d\xi} = \frac{-c_{h^{\cdot}} D_{h^{\cdot}}}{RT} \left(\frac{d\mu_{h^{\cdot}}}{d\xi} + F \frac{d\varphi}{d\xi} \right). \quad (10)$$

With Eqs. (9) and (10), Fick's first law is depicted as modified by Einstein, i.e. the driving force for chemical diffusion is not a gradient in concentration, but rather the gradient in chemical potential or, for ionic solids and liquids, the gradient in electrochemical potential ([1], p. 63). In these equations, c_i is the concentration, η_i the electrochemical potential, and μ_i the chemical potential each of the species i , whereas φ is the electrical potential and F is Faraday's constant (96 485 J/mol/V). The continuity condition is the requirement for charge neutrality:

$$\sum_i z_i j_i = 0 = 2j_{M^{2+}} + j_{h^{\cdot}} \quad \text{or} \quad 2j_{M^{2+}} = -j_{h^{\cdot}}, \quad (11)$$

where z_i is valence. For mode III to be operational, $(c_{h^{\cdot}} D_{h^{\cdot}})$ is much greater than $(c_{M^{2+}} D_{M^{2+}})$; on this basis, one finds that $d\eta_{h^{\cdot}} = 0$ when substituting Eqs. (9) and (10) into Eq. (11): hence, one cannot sustain an electrochemical potential gradient for the electron holes, which is the definition of the semiconductor condition introduced earlier. Concentrating on the divalent-cation flux (Eq. 9), one sees that the chemical potential gradient of an ion species is expressed, specifically $d\mu_{M^{2+}}/d\xi$, which is difficult to control in experiments or in production, as was noted in the Introduction. Knowing how neutral species are formed by reaction of ions with electrons (e.g. $M^{2+} = M + 2h^{\cdot}$) and oxide components by the reaction of metal with oxygen ($M + \frac{1}{2}O_{2(g)} = MO$), one can transform Eq. (9) into a description of mode III oxidation [12]:

$$j_{M^{2+}} = \frac{+c_{M^{2+}} D_{M^{2+}}}{2RT} \frac{d\mu_{O_2}}{d\xi}. \quad (12)$$

This equation is of fundamental importance in understanding mode III oxidation: it proclaims that a chemical potential gradient of oxygen can have, as its primary response, a flux of cations; oxidation needs not require a flux of atomic, molecular, or ionic oxygen.

The operation of mode III oxidation has been demonstrated with ion (Rutherford) backscattering spectroscopy (RBS) (e.g. [12]). These experiments revealed the existence of surface oxide films, which are not represented in Figure 3, whose thickness increases with reaction time, and also the rather sharp boundary of the oxidation front that moves inward. Both the growth of the crystalline surface film (or of divalent-cation concentration in its absence) and that of the divalent-cation-depleted oxidized glass zone follows parabolic kinetics. Further, the rate of growth of $\Delta\xi$ matches well the tracer-diffusion rate for divalent network-modifying cations for the composition/structure of the oxidized glass, which is orders of magnitude faster than that of oxygen tracer diffusion whether by atoms, molecules, or ions [12, 13].

Whereas mode III response is robust, the morphology/texture of the reaction is sensitive to the thermodynamic conditions. A FeO-bearing CaO–MgO aluminosilicate glass ("Fe-CMAS"; no alkali oxides) oxidized in air near its glass transition temperature, for example, results in nm-scale crystalline ferrite ($MgFe_2O_4$) being precipitated at the internal oxidation front; these precipitates exist in a substantially iron-depleted, oxidized glass. In contrast, a basaltic glass (prepared from remelted basalt rock), similar in polymerization to the Fe-CMAS glass but containing ~4.1 mol % of total alkali oxides ($Na_2O + K_2O$), experiences no internal precipitation of ferrite. "Stabilization" of Fe^{3+} as a network former in the oxidized glass occurs instead through incorporation of alkali ions, particularly Na^+ , which had diffused from significant depth in the specimen to the internal oxidation front [12]. For a basaltic liquid subjected to an air environment, however, mode III oxidation still occurs, but the internal interface is the place where the oxygen activity is such that ferrite (Fe_3O_4) becomes a liquidus phase for the temperature of the experiment: the structural changes in the melt wrought by the loss of divalent cations to the free surface changes the liquidus equilibrium (the phase diagram "evolves"): the liquid thus gets supercooled isothermally [13].

There are variations on the theme of reaction modes presented in Figure 3; these depend on the overall chemistry of the glassmelt or glass and/or temperature. As the alkali oxide content of a glassmelt increases, particularly relative to the content of transition metal oxides, the transport coefficient of the alkali ions (particularly $Na^+ \pm K^+$) can, for example, exceed that of the electronic species. Mode III can remain the dominant mechanism, but

the compensating flux becomes that of alkali ions: the oxidized glassmelt changes from an electronic to an ionic or a mixed conductor (e.g. [14]). Again with a sufficient content of network-modifying alkali or alkaline earth oxides, the dynamics can evolve to mode II as temperature increases, with a compensating flux provided by cations instead of by $h^\bullet$ (e.g. [15]). The shift to mode II with increasing temperature is straightforwardly understood: the activation energy for mobility of O^{2-} is greater than that of the network-modifying cations. One consequence is that at high enough temperature the mobility of O^{2-} will exceed that of the network-modifying cations, and thus the O^{2-} transport coefficient becomes dominant. Molecular O_2 also sees its mobility increase rapidly with temperature [15]. A change of redox dynamics to mode I is unlikely for most multicomponent silicates, however, due to the limited solubility of the gas keeping the O_2 transport coefficient relatively small.

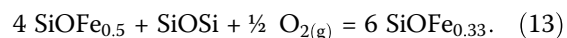
4.2 A Structural Perspective on Open-System Oxidation Dynamics

As noted above, mode III oxidation of glassmelts and glasses is similar to that observed in crystalline oxide or silicate solid solutions. In $(Fe,Mg)O$ (magnesiowüstite) and $(Fe,Mg)_2SiO_4$ (ferromagnesian olivine), as examples, the physical manifestation of the oxygen activity is the coupled concentrations of negatively charged vacancies on the divalent-cation sublattice, which are denoted by $V''_{M^{2+}}$ (NB. the subscript denotes the sublattice and the superscript charge – a prime is a negative charge; here there are two of them), and electron holes, which physically are Fe^{3+} present on the divalent-cation sublattice ($h^\bullet \equiv Fe^\bullet_{M^{2+}}$). The concentrations are coupled by the requirement of charge neutrality, specifically $[h^\bullet] \cong 2[V''_{M^{2+}}]$, where the brackets denote the number of defects per molecule on the lattice, a unitless concentration. As the oxygen activity increases, the concentration of both defects increases: $[h^\bullet], [V''_{M^{2+}}] \propto p_{O_2}^m$ where $m \sim 1/6$ ([1], p. 171). In the oxidation of these (and similar) Fe^{2+} -bearing crystalline compounds, then the hole and vacancy concentrations are higher at the free surface and lower in the interior. Holes and vacancies thus flux inward, whereas the geometric requirement that a vacancy exchange with an ion on its sublattice imposes a divalent-cation flux outward: mode III. It is important to note that the motion of $h^\bullet$ does not require the diffusion of Fe^{3+} ions; rather only the electron is moved from one iron ion to another, which is a much faster and lower-energy process. Nevertheless, the defect $Fe^\bullet_{M^{2+}}$ causes a local distortion in the crystal structure, a “small polaron,” which tracks with the motion of the electron hole; the diffusion process is described as polaron

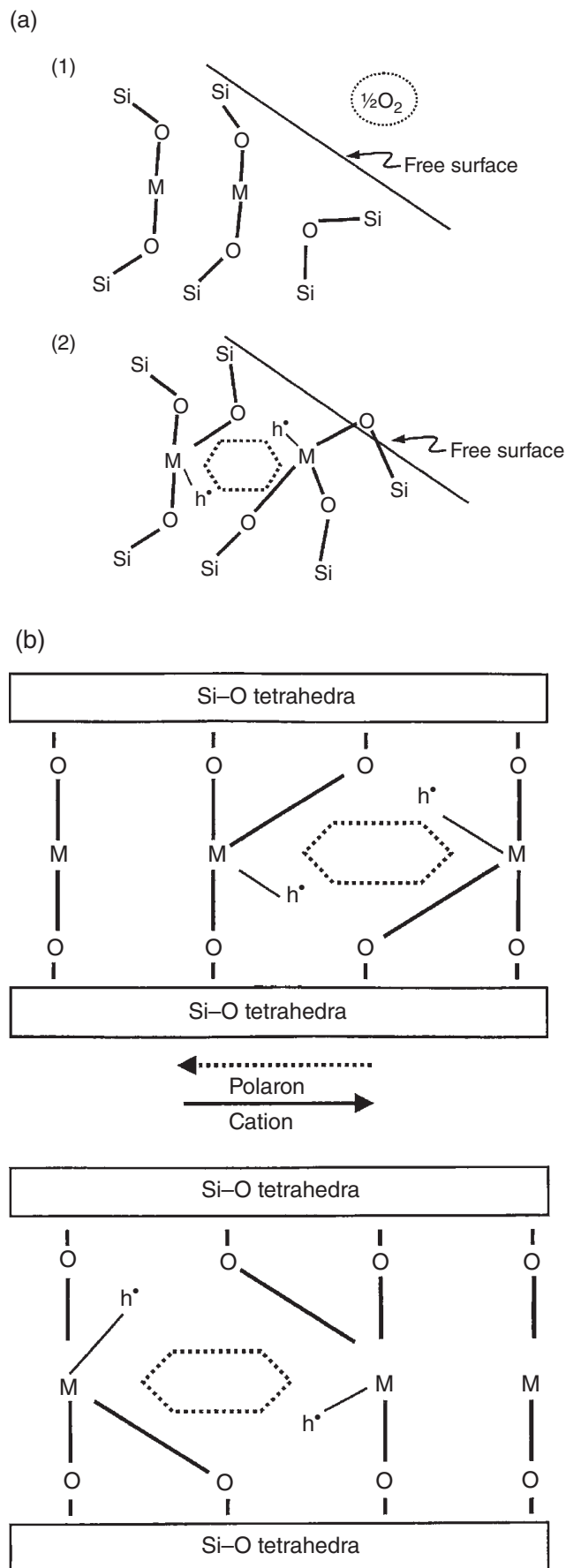
hopping and is characterized by a Boltzmann statistics that is similar to that of ionic diffusion.

Of course glassmelts and glasses have neither a lattice nor sublattices. But they do have an atomic structure, and mode III oxidation response of network-modifying cation motion against a relatively immobile aluminosilicate network evokes parallels to point-defect phenomena. The structure of amorphous silicates is described statistically: bond lengths and bond angles have distributions. Defects, then, can be viewed as extraordinary bond lengths and angles, a perspective originally championed by Schaeffer [16]. Based on dynamical similarities between the amorphous and crystalline states, one may anticipate the creation of such defects at equilibrium concentrations of a part per thousand, atomic, or less. The defect concentrations, being functions of both temperature and chemical potential(s), can be characterized through chemical equilibria. One effective approach to this end is an application of the polymerization model of Hess [8].

The Hess model evaluates polymerization of amorphous silicates by paying particular attention to the bonding environments of oxygen anions: structural elements in reactions are described by having the bonds to each O^{2-} characterized by a summed Pauling bond strength (electrostatic valence) of two; these elements are then used to write reactions that are balanced both in matter and in charge. For example, in the case of the oxidation of a glass or glassmelt at its free surface, network-modifier Fe^{2+} reacts with atmospheric oxygen to create network-modifier Fe^{3+} ; in Hess notation,

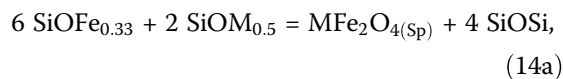


In reaction (13), SiOSi represents a bridging oxygen, $2 \text{ SiOFe}_{0.5}$ represents a network-modifier Fe^{2+} , which provides one positive charge to each of two O^{2-} , and $3 \text{ SiOFe}_{0.33}$ represents a network-modifier Fe^{3+} , which is the manifestation of an electron hole, or small polaron, in the amorphous structure. By inspection, one sees that reaction (13) is atomically balanced. The reaction is charge-balanced as well: two Fe^{2+} cations have provided one electron each to ionize the neutral oxygen atom, which is then bonded to the amorphous silicate. The reaction is depicted schematically in Figure 4a, whose part (1) represents the left side of the equilibrium and part (2) the right, Fe^{2+} being represented by the generic M. One easily imagines that the bonding of the oxidized iron ($Fe^{3+} \equiv M-h^\bullet$ in the figure) to three O^{2-} anions instead of Fe^{2+} to two anions distorts locally the structure of the glassmelt/glass; in Figure 4, this feature is depicted as a polyhedral void. Nevertheless, one understands that as the electron holes migrate inward, the distortion travels with them and divalent cations are displaced in the opposite direction (Figure 4b): in the kinetic response, the

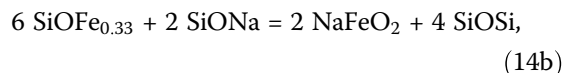


distortion acts effectively as a “vacancy” in the amorphous structure. As suggested by Greaves [17], Figure 4b additionally assumes a percolative nature for the spatial distribution of network-modifying oxide components in the amorphous state; such an interpretation is consistent with the redox reaction textures of sufficiently depolymerized melts/glasses [11, p. 317].

One can infer from reaction (13) that the oxidation reaction is depolymerizing because the bridging oxygen unit Si–O–Si is consumed. This is counter to experience according to which oxidized glassmelts increase in polymerization and so in viscosity. But it must be emphasized that reaction (13) is actually a “half reaction,” that is, the overall oxidation reaction is the sum of two half reactions, one at/near the free surface (depicted in Figure 4a) and the other at the internal reaction front, the two half reactions mediated and rate limited by chemical diffusion ([1], p. 104). As described above for some non-alkali oxide-bearing glasses, the reaction at a temperature near the glass transition causes precipitation of nm-scale ferrite at the internal interface. The simplified version of this half reaction, in Hess notation, is



where M here is either Mg^{2+} or Fe^{2+} (i.e. the magnesioferrite–magnetite solid solution; the subscript “Sp” standing for crystalline spinel). Here one sees the formation of four bridging oxygens as three network-modifying cations are extracted from the solution (plus the requisite amount of O^{2-}) to form the crystalline ferrite. In glasses with alkali oxides, Fe^{3+} tends to have a network-former status, charge-compensated by a localized alkali ion that no longer fulfills a network-modifier role. Taking Na^+ as the alkali species, one simplifies in Hess notation this half reaction as



where NaFeO_2 represents the network-forming Fe^{3+} [8]; six bridging oxygens are formed in the consumption of eight nonbridging oxygens. A summation of reaction

Figure 4 Schematic illustration of small polaron dynamics in silicate glassmelts and glasses [13], with structural units based on the melt polymerization model of Hess [8]. M is a divalent network-modifying cation; M–h[•] is a trivalent network-modifying cation. (a) Formation of a small polaron via oxidation (cf. reaction (13)): (1) unreacted glass/glassmelt and (2) formation of a polaron as two divalent network modifiers become trivalent network modifiers as atmospheric oxygen accepts two electrons and bonds into the glass/glassmelt as O^{2-} . The structural distortion so created follows the migration of the h[•]. Note also the consumption of a bridging oxygen (Si–O–Si): this near-surface (half) reaction is depolymerizing. (b) Migration of a small polaron, and the associated (counter) motion of the network-modifying cation, in a transition metal-bearing silicate glass/glassmelt.

(13) with either reaction (14a) or (14b) illustrates a definite net increase in polymerization for the oxidized glass/glassmelt.

The simplification in reactions (13) and (14) is that each half reaction must have as a product the mobile species that “communicate” the oxidation potential between the external and internal interfaces. The free-surface reaction, reaction (13), clearly produces $2h^*$ ($\equiv 6 \text{ SiOFe}_{0.33}$), which diffuse inward; a more complete description of reaction (14a and b) at the internal interface must include the fact that the structural relaxation that results in precipitation of ferrite or in incorporation of Fe^{3+} as an alkali-ion-compensated network former must also “release” divalent network modifiers to diffuse toward the free surface. These more complete reactions are described in [12] and in the references cited there.

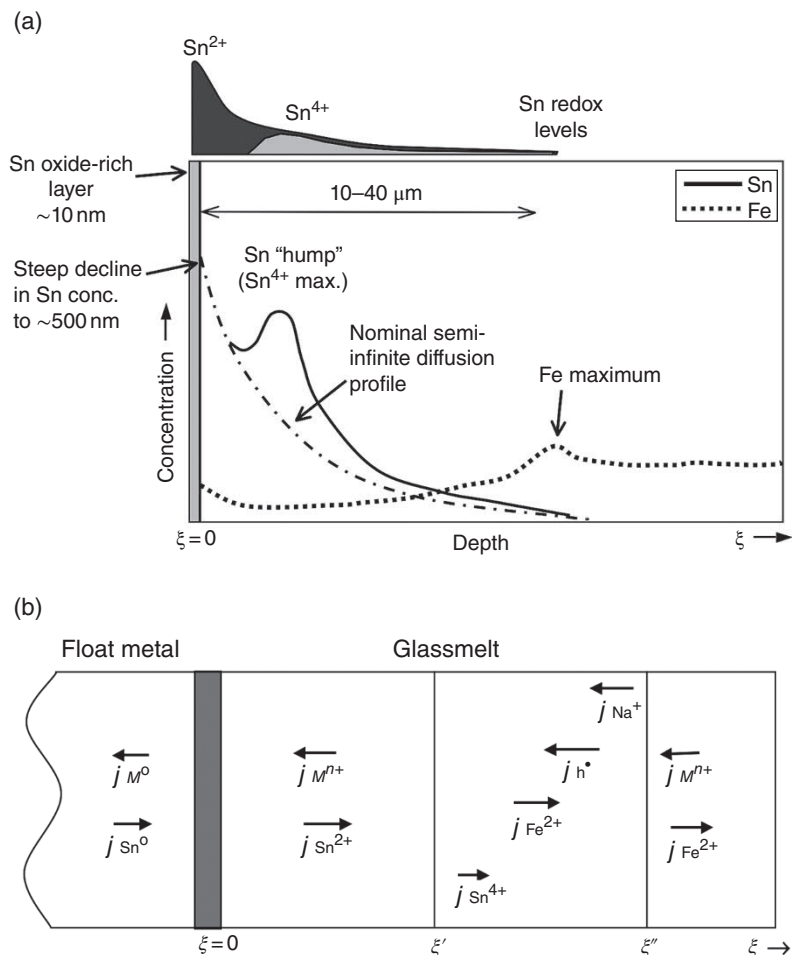
4.3 Open-System Reduction and the Float-Glass Reaction

Under some circumstances, dynamic reduction can be understood as the mirror image of the oxidation process. Specifically, O^{2-} is chemically ablated (i.e. by reaction with neutral species in the atmosphere) from the free

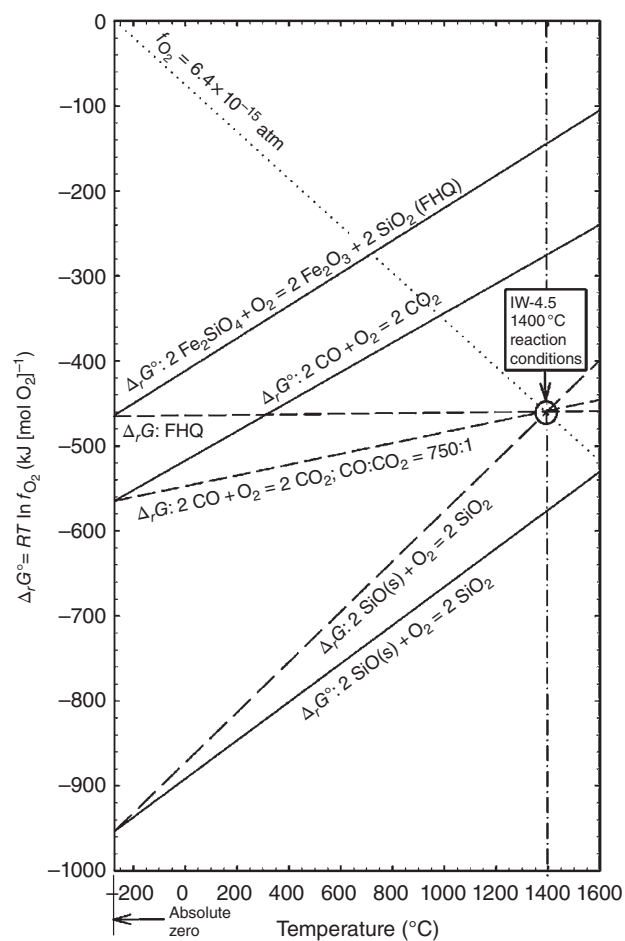
surface in a half reaction that consumes h^* ; the reaction both decreases the activity of h^* and increases the activity of divalent-cation oxides at the free surface, impelling outward diffusion of h^* and inward diffusion of M^{2+} network-modifying cations. These dynamics are essentially the reverse of reaction (13) and of Figure 4a, i.e. consider the compound figure in the order (2) $\rightarrow$ (1). Structural relaxation of the glassmelt/glass occurs at an internal interface, one that shifts ever deeper, following parabolic kinetics. Depending upon the thermodynamic conditions, the internal reaction can yield, too, precipitation of nm-scale precipitates of metal ([11], p. 326).

The foundation of the float-glass reaction, from the perspective of the glassmelt ribbon, is dynamic reduction that is accompanied by solution formation; the metallic float medium experiences oxidation and solution formation, but this side of the reaction is not rate limiting and so is ignored here. The thermodynamics was articulated in Section 2.2 and illustrated in Figure 2. At the molten tin/glassmelt interface, tin is oxidized through electron donation to cations in the silicate, which are reduced: Sn^{2+} then is incorporated into the glassmelt, and metallic Na (particularly), Si, Fe (a minor component of NCS glass), and Ca are added in various amounts to the tin bath. The reaction texture is telling (Figure 5a).

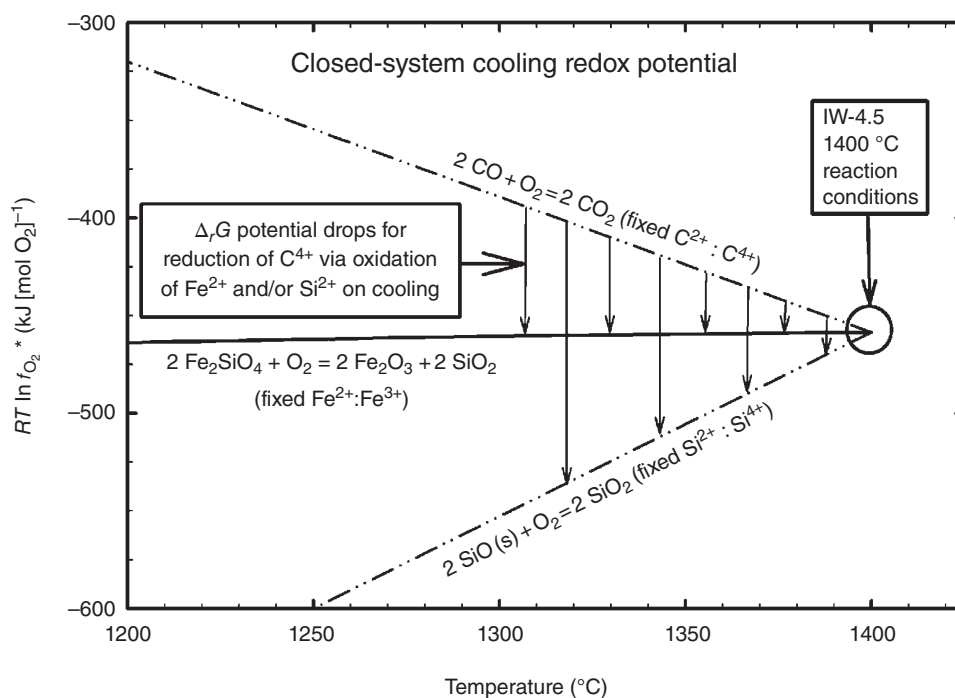
Figure 5 Open-system redox dynamics in the NCS-on-Sn float-glass process [6]. (a) Schematic summary of chemical observations of ionic Sn and Fe in the near-float-surface region ($\sim 50\text{--}100 \mu\text{m}$) of the glassmelt ribbon. Ionic Sn is concentrated in the first 500 nm and then assumes a Fickian compositional profile, but one punctuated with an anomalous buried hump. Ionic Fe is depleted in the region of Sn diffusion, but shows an anomalous maximum near the depth limit of Sn penetration. Sn^{2+} is the dominant Sn oxidation state at/near the surface, giving way to Sn^{4+} at the position of the Sn hump (see top of schematic). The concentration humps for Sn and for Fe are evidence of two internal redox couples effecting local structural change in the glassmelt. (b) Schematic of fluxes (with senses shown) and internal reaction fronts (ξ' and ξ'') active in the glassmelt/float-metal reaction, consistent both with the chemical profile presented in (a) and with an understanding of dynamic reduction effected by cation diffusion.



(a)



(b)



Employing a variety of analytical techniques, surface-science studies of the float-bath side of the glassmelt ribbon reveal Fick's second law diffusion profile for ionic Sn extending into the silicate. This profile, however, is punctuated by an anomalous Sn-concentration hump, which is distinctly inconsistent with simple diffusion-effected solution formation [6]. Near the end of ionic Sn penetration, one also finds an anomalous hump of the ionic Fe concentration. These humps are unequivocal evidence of reaction-effected changes in the internal atomic structure of the glassmelt, both of which are related to redox dynamics. Referring to the schematic geometry depicted in Figure 5b, one sees that the Sn hump corresponds to a location where Sn^{2+} , a reasonably mobile network modifier, is oxidized to Sn^{4+} , which, if still too large a cation to be a network former, will have a notably diminished mobility compared with Sn^{2+} in the glassmelt. The location of this internal interface ($\xi = \xi'$ in Figure 5b) corresponds to the position where the activity of SnO is sufficiently high to drive a redox couple where 2h^+ are consumed in the creation of Sn^{4+} . This reaction creates a "sink" for h^+ at ξ' , which is dealt with by a flux of h^+ emanating from the deeper interface ξ'' , the site of the internal reduction reaction. At ξ'' , reaction (14b) is driven from the right to the left, i.e. Na^+ -compensated network-former Fe^{3+} is reduced to a combination of network-modifier Fe^{3+} ($\equiv \text{h}^+$), network-modifier Fe^{2+} , and network-modifier Na^+ . The physics of the reactions and the nature of the fluxes depicted in Figure 5b are justified in Ref. [6]. As evidence in its favor, we have employed this analysis to demonstrate distinct control of the kinetics of the float reaction by (i) doping the glassmelt with additional electron acceptors (Fe^{3+}), (ii) alloying strongly the float medium (i.e. to lower the activity of Sn), and (iii) replacing Sn altogether in the float medium with an alloy whose oxidizable component, when fully ionized, assumes a definite network-former role within the glassmelt (e.g. Ge).

5 Closed-System (or Internal) Redox Dynamics

The other end-member dynamics are where diffusion beyond the molecular scale is not anticipated because of either (i) sluggish kinetics at low temperature or (ii) little time spent at an elevated temperature. The extreme situation of this type is thermal quenching, where the thermal diffusivity and heat flux outstrip the transport coefficient of any atomic/ionic component of the system. In such situations, the composition of the glassmelt/glass cannot change, but the redox potentials can because of the relative temperature effects on the activity coefficients of the components.

This evolution of the redox potentials is illustrated with an Ellingham-diagram analysis in Figure 6, which compares open- and closed-system thermodynamics for an iron-oxide-bearing calcium-magnesium aluminosilicate melt that has been driven to equilibrium with a very low oxygen activity [18]. The condition where $T = 1400^\circ\text{C}$ and the oxygen activity is controlled and sustained at 6.4×10^{-15} (i.e. an ambient-pressure fugacity of $f_{\text{O}_2} = p_{\text{O}_2} = 6.4 \times 10^{-15} \text{ atm}$) is noted in Figure 6a as the center of the small circle, nominally at the right center of the diagram, whose ordinate is $-460 \text{ kJ}/(\text{mol O}_2)$. This condition is highly reducing; the oxygen activity is four and a half order of magnitude below that for the reaction between metallic iron and the mineral wüstite ("IW-4.5") for this temperature. In this example, the oxygen activity is created and sustained by dynamic mixing and reaction of $\text{CO}_{(\text{g})}$ and $\text{CO}_{2(\text{g})}$ at a ratio of 750 : 1; thus, beyond setting the oxygen activity, the glassmelt at equilibrium must incorporate carbon oxides in forms that include physically dissolved molecular species (i.e. present in the free volume of the melt) as well as chemically dissolved ionic/covalent species (i.e. incorporated into the structure of the glassmelt as, e.g. carbonate, carbonyl, or even

Figure 6 Thermodynamic analysis associated with open-system reduction and closed-system (internal-redox-couple) quenching [18]. (a) Ellingham diagram drawn to demonstrate equilibration of an iron-oxide-bearing calcium-magnesium aluminosilicate glassmelt held at 1400°C and maintained at an oxygen activity (fugacity, f_{O_2}) of $6.4 \times 10^{-15} \text{ atm}$. In this example, the low-oxygen-fugacity environment was set by dynamic mixing of carbon monoxide and carbon dioxide at a ratio of $\text{CO} : \text{CO}_2 = 750 : 1$; at 1400°C , this produces an f_{O_2} that is four and a half order of magnitude lower than the iron-wüstite buffer, i.e. "IW-4.5." Equilibrium requires that each and all of the $\Delta_r G^\circ$ curves (solid lines) must rotate – that is, all activities are adjusted (cf. Eq. (4)) – such that all $\Delta_r G$ curves (dashed lines) converge at the thermodynamic conditions. In the figure, the only $\Delta_r G^\circ$ and $\Delta_r G$ lines presented are those involving heterovalent cations – $\text{C}^{2+,4+}$, $\text{Si}^{2+,4+}$, and $\text{Fe}^{2+,3+}$. The reaction depicted as fayalite-hematite-quartz (FHQ) is used for the Fe^{2+} – Fe^{3+} equilibrium, consistent with the solution model MELTS [10]. (b) A close-up of Ellingham "space" for quenching. From the equilibrium condition, one evaluates an effective oxygen potential (fugacity, $f_{\text{O}_2}^*$) by holding the mole fractions constant – the definition of quenching – but allowing the activity coefficients to change with temperature. The solid curve is the effective oxygen potential calculated for the FHQ reaction directly from MELTS. The dash-dot-dot curves are logical postulates based upon limited solution data for $\text{Si}^{2+,4+}$ and $\text{C}^{2+,4+}$. The divergence of the curves demonstrates that there develops a potential upon cooling to reduce C^{4+} to C^{2+} through a redox couple that oxidizes Fe^{2+} and/or Si^{2+} . The extent of these reactions in reality (in this case, causing bubbles of $\text{CO}_{(\text{g})}$ to form, C^{2+} being especially insoluble in aluminosilicate melts) depends on the thermal history, particularly the cooling rate.

carbide species). Equilibrium with the open system requires all of the component oxide $\Delta_r G(T)$ curves (lines) to converge at the aforementioned condition. Some of the Ellingham $\Delta_r G^\circ(T)$ lines rotate clockwise, some counter-clockwise. Most of the rotation is based on the activity effects of forming the glassmelt solution, although the impact of oxygen activity on curve rotation is significant.

In the analysis of quenching, one determines an “effective” oxygen activity, presented in Figure 6b as an effective fugacity, $f_{O_2}^*$, by holding mole fractions fixed but evaluating the potential based on the temperature sensitivities of the various activity coefficients ([3], p. 240). Consider the $Fe^{2+}-Fe^{3+}$ equilibrium. Because fayalite and hematite are the components representing ferrous and ferric iron, respectively, in the MELTS solution model [10], the reaction of interest is fayalite (Fa) being oxidized to hematite (Hm) plus quartz (Q): $2Fe_2SiO_4 + O_{2(g)} = 2Fe_2O_3 + 2SiO_2$ (“FHQ”). The mass-action relationship for the glassmelt is

$$\begin{aligned}\Delta_r G_{1400^\circ C} &= -460 \text{ kJ} [\text{mol } O_2]^{-1} \\ &= \Delta_r G_{T, FHQ}^\circ + RT \ln \\ &\quad \left[\frac{(\gamma_{Hm}^2 X_{Hm}^2)(\gamma_Q^2 X_Q^2)}{(\gamma_{Fa}^2 X_{Fa}^2)(f_{O_2}^*)} \right],\end{aligned}\quad (15)$$

where X_i is the mole fraction and $\gamma_i (= \gamma_i(T))$ is the activity coefficient, both of species i in the glassmelt solution, and $f_{O_2}^*$ is in units of atm (i.e. the oxygen term becomes unitless by its normalization to 1 atm). The calculation is “pinned” to the condition where equilibrium was established at 1400 °C.

As temperature is lowered, $\Delta_r G_{FHQ}^\circ$ evolves as do the γ_i ; holding the X_i fixed at their values of the original 1400 °C equilibrium allows calculation of $f_{O_2, FHQ}^*(T)$, which is shown as the FHQ* solid line in Figure 6b. The slope of FHQ* is steeper than the FHQ curve in Figure 6a. Given good solution models, similar calculations might be done for the CO/CO₂ and SiO/SiO₂ equilibria, which, unfortunately, have not been calibrated. The dash-dot-dot curves in Figure 6b are thus drawn based on inferences from the literature concerning the solubilities of the various species in an alkaline earth aluminosilicate melt. One sees that, with increased cooling, a greater and greater potential develops for the reduction of C^{4+} to C^{2+} by acceptance of electrons from Fe^{2+} and Si^{2+} . Whether the redox-exchange reaction is realized, of course, depends on the kinetics of cooling and on any subsequent thermal treatment. Since the redox exchange is accompanied by structural relaxation of the glassmelt or glass, the kinetics will be phonon assisted, again following Boltzmann statistics.

The thermodynamics described in Figure 6b can be applied to decipher a variety of phenomena encountered in glassmaking and also to understand the structure and chemistry of melts from studies of quench specimens.

Brightly colored “ruby” glasses are created by the precipitation of noble (e.g. Au) or relatively noble (e.g. Ag, Cu) colloidal metal via “striking,” i.e. driving a closed-system redox exchange by reheating a formed, often colorless glass (Chapter 6.2). In gold ruby glasses, the gold in the high-temperature glassmelt exists in ionized form ($Au^+ \pm Au^{3+}$). To produce colloidal metal, a reducing agent is added, a typical one being SnO, although oxides of Se and Te have been used historically as well [19]. The thermodynamics of striking are directly analogous to the closed-system C–Si–Fe redox couples presented in Figure 6b. Reheating and holding the glass at a temperature below its original melting/solution temperature, usually between the annealing and softening points, provokes the redox exchange $Au_2O + SnO = 2 Au + SnO_2$; the magnitude of the $\Delta_r G$ exchange potential allows the barrier to crystal nucleation to be overcome. The “soak” time of anneal is selected to effect growth of the colloidal metal crystals so as to achieve the desired color and saturation. The growth process is an Ostwald ripening. Its slowness is due to the insolubility of metal atoms in the silicate solution, since diffusion through the silicate is accomplished by ions and not by atoms ([20], p. 723).

These very same physics effect the precipitation of Pt metal inside quenched melts that are initially prepared in platinum crucibles or in Pt-lined production furnaces [7]. Platinum, too, dissolves into glassmelts as an ionic species ([20], p. 723); as a consequence, melts with as high a polymerization as practicable that are melted in a reducing atmosphere minimize the incorporation of Pt^{2+} and Pt^{4+} and so the potential for its internal reduction into metal precipitates [7].

In contrast, the solubility of platinum-group elements (PGE: Ru, Rh, Pd, Os, Ir, and Pt) in highly depolymerized, high-temperature aluminosilicate melts is of particular interest with regard to understanding the chemistry and physics of terrestrial planetary differentiation and core formation. For years, this solubility was underestimated because of the formation of PGE metal “micronuggets” within the quenched experimental charges: this metal was not understood to have precipitated as a result of a closed-system redox reaction such as described here. The correct explanation has been arrived at through clever experiments under extreme conditions (2500 °C; 2.2 GPa), whereby a highly MgO- and FeO-rich aluminosilicate melt was reacted with platinum metal in the context of containment within a graphite capsule. When the melt experienced sufficiently rapid cooling and a

sufficient cooling-rate gradient, the redox-effected precipitation of metal and of $\text{CO}_{(\text{g})}$ in the more slowly cooled regions of the charge could be observed along with the high solubility of ionic Pt and C corresponding to the experimental conditions [21]. The carbonate (or carbonyl) reduction to $\text{CO}_{(\text{g})}$ follows exactly the physics depicted in Figure 6b.

The removal of gas bubbles or “seed” by fining of glassmelts has long involved application of redox agents, particularly $\text{As}^{3+,5+}$ and $\text{Sb}^{3+,5+}$, a practice that is now less frequent owing to environmental and worker-health concerns and also, in the case of glass used as substrates for electronic displays, because of chemical incompatibilities between these group 15 metalloids and silicon- or germanium-based circuitry. The pentavalent oxides added to the glass batch are reduced to the trivalent state during melting. For many years, the release of oxygen gas by the reaction, e.g. $\text{As}_2\text{O}_5 = \text{As}_2\text{O}_3 + \text{O}_{2(\text{g})}$, was thought to facilitate the gravity-driven migration of bubbles to the free surface. Given the small amount of pentavalent oxide added to the batch, however, calculations of Stokes’ flow dynamics of bubbles so produced suggest that this reaction represents a minor contribution to fining. Rather, the re-oxidation to the pentavalent state at a lower temperature can absorb oxygen from the bubbles and thus cause them to shrink [22, 23].

Overall, the physics of fining are a convolution of the open- and closed-system cases presented above. Again, one can understand the driving potential for the trivalent-to-pentavalent oxidation reaction in a way consistent with the closed-system description of Figure 6b, but at issue is the amount of physically dissolved $\text{O}_{2(\text{g})}$ in the glassmelt. As the glassmelt cools, thermal contraction reduces the free volume of the melt; consequently, the chemical potential of the physically dissolved $\text{O}_{2(\text{g})}$ increases. Re-oxidation of the fining agent consumes some of this physically dissolved oxygen through its incorporation into the melt structure as O^{2-} and so affects locally the structure of the glassmelt. The modified glassmelt can thus accept more $\text{O}_{2(\text{g})}$ molecules from the bubble, shrinking it. This situation is similar, of course, to the surface reactions associated with an open system. Kinetic models for bubble shrinkage in the reaction so described employ a simple Fick’s second law approach but are only partially successful: despite being rate limited by diffusion of molecular oxygen, the dynamics probably has more in common with the open system as depicted as mode I in Figure 3, where the internal interface is the place where the trivalent-to-pentavalent reaction and structural relaxation occur.

Particularly in NCS glassmelts, an additional aspect of the fining process is that the Na_2O and CaO components are frequently introduced as carbonates in the batch.

Breakdown of these carbonates produces $\text{CO}_{2(\text{g})}$, which makes up a significant component of the gas bubbles to be removed in fining. Again, consistent thermodynamically with Figure 6b, redox couples between the CO_2 and the trivalent metalloid oxide component in the glassmelt oxidize the metalloid to the pentavalent state while producing $\text{CO}_{(\text{g})}$, whose transport coefficient through the glassmelt to its free surface is much, much greater than that of $\text{CO}_{2(\text{g})}$ ([24], p. 210).

6 Perspectives

The bulk properties of glasses such as color, electronic and ionic conductivity, viscosity, etc. are directly related to atomic-level structure and, thus, to ion valence. Endowing a bulk glass with specific properties via internal (closed-system) redox couples is a thermochemical design problem of broad flexibility because it makes available control of chemical activities via composition and of cooling-effected driving potentials in both post-melting and post-forming processing; optimal protocols can be identified via multivariable experimental design. More intriguing, however, are the possibilities of open-system redox in affecting/effecting electro-optical response in glass at or near the free surface. Consider, for example, a processing approach whereby the float bath is alloyed with transition element or rare earth metals so as to incorporate these in the near surface of the glassmelt via redox exchange. Depending on the initial composition of the glassmelt, the combination of redox exchange and solution formation can produce not just one specific location of a controlled local structure (like the Sn hump in conventional NCS float glass; Figure 5a) but multiple layers of such structure, i.e. redox-effected Liesegang banding. Optical interference and amplification are potential responses that can be so controlled.

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5.7

Optical Basicity: Theory and Application

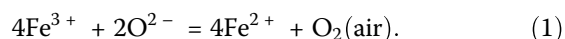
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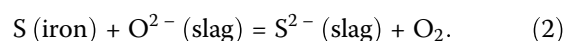
1 Introduction: The Need for a Suitable Basicity Scale for Oxide Melts

Ordinary glass is made by heating a mixture of basic oxides, Na_2O , CaO , etc. with SiO_2 . The vast range of possible compositions allows much scope for optimizing properties such as refractive index or color, mechanical strength, or high-temperature chemical reactivity. Extensive correlation studies have shown convincingly that properties of the glass or melt rely heavily on chemical composition in terms of basicity (basicity rather than acidity, because usually bases are the focused variable).

For many years, however, the quantifying of basicity was a frustrating problem. Probably the most serious limitation to progress was to disregard the fundamental difference of the O^{2-} ion compared with other monatomic anions that are usually encountered in solution chemistry. These are singly charged, but for oxygen, addition of a second electron to the already charged O^- ion is thermodynamically unfavorable. In the present context, this questions the viability of the O^{2-} species. The seriousness of this problem is illustrated by the questionable adoption of the Lux-Flood theory (a discussion of which is in [1]) together with its analogy of $p(\text{oxide})$ with pH and also by the improbable anionic counterions suggested for redox equilibria. As illustrated by many examples, redox reactions impinge greatly on molten salt chemistry. Thus, for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion couple in the manufacture of glass, the equilibrium might be written as



Likewise, the refining action of metallurgical slags can be described by



Thermodynamic approaches to such equilibria are not straightforward. Indeed, Eq. (1) suggests that increasing melt basicity favors the lower oxidation state cation, whereas experimentally one usually observes the reverse.

There was much research effort attempting to deal with the problems, especially in view of their technological importance. Overall, the literature of the time (up to the 1970s), and meetings of professional groups, reflected notable conflict. What was needed was a chemically convincing theory with a numerical scale that would facilitate meaningful comparisons between, say, a sodium silicate, a potassium silicate, and a sodium borate melt. Trends in physical and chemical properties would then be linked directly to this *common* scale rather than to chemical constitution. Such a scale was eventually provided in 1971 with the introduction of the optical basicity theory [2].

2 Theoretical Foundation of Optical Basicity

With the concept of optical basicity, one considers an oxide glass or crystal in artificial terms as an array of its constituent cations, Na^+ , Ca^{2+} , Si^{4+} , ... and O^{2-} ions. Chemical bonding between these species, which can be described as Lewis acid–base neutralization, uses much of the negative charge on the oxygen. It is the remaining charge that chiefly causes those properties of the glass that are recognized as its basicity. Because this residual charge varies markedly with cation composition, it is the measuring of these changes in electronic charge that is at the heart of optical basicity.

To achieve this goal, probe cations are dissolved in the molten glass. They were specially chosen, so when they are coordinated by the oxygen atoms of the glass, they

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would signal fundamental features of the chemical bonding. Transition metal ions can be seen as an obvious choice because their bonding is understood in terms of molecular orbital theory (which, as the ligand field theory, had been purposefully developed for inorganic coordination chemistry during the years leading up to ~1950). Their d–d spectra, obtained using conventional UV/visible/near-infrared (optical) spectroscopy, reveal a decrease in repulsion energy between the electrons in their d-level. It is this effect that concerns the optical basicity model because, vitally, it provides a simple description of the chemical bonding between the probe ion and the oxygen atoms of the glass. For transition metal complexes, chemical bonding generally results in the d electrons experiencing greater shielding from the positive nucleus, extra to that provided by the core electrons. Consequently the d orbitals expand and the d–d repulsion decreases. It was C.K. Jørgensen who referred to this expansion as the *nephelauxetic* effect [3].

The repulsion between the d electrons is expressed as the Racah B parameter. For the free uncombined metal ion, this important energy (frequency, B_f) is known from its atomic spectrum, which is published in standard tables. When the metal ion is complexed by the ligands and the orbitals expand, B_f falls to B_{complex} . Since B_f represents 100 % ionicity, decreasing B can be taken as the introduction and increase of covalency within the bond between the ligand and metal ion. Jørgensen assigned the proportional reduction of the Racah parameter, i.e. the ratio $(B_f - B_{\text{complex}})/B_f$, to the contributions of ligand and metal ion (parameters h and k) such that

$$\frac{(B_f - B_{\text{complex}})}{B_f} = h k. \quad (3)$$

The h parameter was set at unity for the H_2O ligand in crystalline aqua complexes such as $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, etc. The d–d absorption spectra of these complexes allow the parameter k to be derived for each metal ion. With these parameters to hand, one can then determine the values of h for Cl^- , NH_3 , ... from the spectra of chloro, ammine, and other complexes. The set of h and k values shows good consistency on going from one complexed metal ion to another. For what would be the *optical basicity* model, the strategy adopted is to restrict the donor atom to oxygen (always in the oxidation state of -2 and denoted oxide(-II)), and therefore to regard the coordination by the aqua ligand as a particular case for oxide(-II) ligands. In short, this scheme has the great interest in allowing the complexation of metal cations by silicate, borate, etc. to be considered in terms of molecular orbital theory, that is, in terms of the nephelauxetic effect.

In practical terms, however, obtaining B_{complex} from d–d absorption spectra is complicated. Fortunately, past

investigations have shown that one can avoid much difficulty by using instead the s–p spectra of $(n-1)d^{10}ns^2$ metal ions such as Pb^{2+} and Tl^+ [4]. Their UV absorption bands, which arise from transitions to the $(n-1)d^{10}ns^1np^1$ configuration, are Laporte allowed and very intense, even for the nominally spin-forbidden $^1S_0 \rightarrow ^3P_1$ band. This band has the lowest energy and usually presents itself with a clearly defined frequency maximum, which we label ν . Significantly, this frequency has features in common with B_{complex} so that it can be used for estimating covalency changes in the oxide(-II) bonding with the metal ion. For example, the frequency ν is linearly proportional to the h parameters of Cl^- , Br^- , NH_3 , etc. However, since the frequency shifts for the variation of B_{complex} on the one hand and the $^1S_0 \rightarrow ^3P_1$ ($6s \rightarrow 6p$) on the other arise from very different mechanisms, the extrapolated frequency values of ν_f for the Pb^{2+} and Tl^+ ions in the free gaseous state (that is when h is zero) will not necessarily be exactly the experimental values. Indeed, this was found to be the case, with ν_f equal to $60\,700\text{ cm}^{-1}$ for Pb^{2+} and $55\,300\text{ cm}^{-1}$ for Tl^+ (experimental values for the free ions being, respectively, $64\,391$ and $52\,393\text{ cm}^{-1}$). These optical-spectroscopy results and others [4] were regarded as promising for constructing an acid–base scale suitable for measuring the basicity of melts and glasses.

Already there is a defined zero, which is the free ion value of the $^1S_0 \rightarrow ^3P_1$ frequency, ν_f , for $(n-1)d^{10}ns^2$ ions – admittedly an “adjusted” free ion value. Initially, attention was directed mainly toward the Pb^{2+} ion on which to construct the basicity scale (although the Tl^+ and other ions were also used). In order to avoid the many problems associated with the idea of “100 % covalency,” pragmatically crystalline calcium oxide was chosen for unit optical basicity. The Pb^{2+} ion in the highly basic CaO environment has its $^1S_0 \rightarrow ^3P_1$ band frequency, ν_{CaO} , at $29\,700\text{ cm}^{-1}$, and hence the frequency range from 100 % ionicity to the CaO environment, $(\nu_f - \nu_{\text{CaO}})$, is $60\,700 - 29\,700\text{ cm}^{-1}$, i.e. $31\,000\text{ cm}^{-1}$. Writing ν_{medium} for the probe-ion frequency in the medium under investigation, for example, a glass, one defines the optical basicity, Λ , by analogy with the Racah B parameter as the proportional energy change, $(\nu_f - \nu_{\text{medium}})/(\nu_f - \nu_{\text{CaO}})$ [2]:

$$\Lambda = \frac{(60\,700 - \nu_{\text{medium}})}{31\,000}, \quad (4)$$

or, for when Tl^+ is used,

$$\Lambda = \frac{(55\,300 - \nu_{\text{medium}})}{18\,300}. \quad (5)$$

When the probe ion is added to the melt (e.g. as a 10^{-3} molar nitrate), the salt readily decomposes, and the metal ions occupy the sites presented by the network medium (we can usually ignore the small quantity of oxide(-II) that

is generated). An example of the use of Eq. (4) is for Pb^{2+} dissolved in a sodium borate (20 mol % Na_2O) glass (Figure 1), where ν_{medium} is $45\,000\text{ cm}^{-1}$ and therefore $\Lambda = 0.51$. Usually although not always, optical basicity is quoted to two decimal places, but for comparative purposes it can be useful to have three places. Of course, it is necessary that the glass has good UV transparency, although fluorescence spectroscopy can also be used for lower-quality samples.

With the accumulation of optical basicity data for a variety of glasses, the next step is to consider how Λ is related to chemical constitution. In addressing this question, we return to the artificial model, which is the starting point of optical basicity, and consider how the array of oxide(-II) ions becomes neutralized by the constituent cations. For example, in the glass CaO-SiO_2 (40 : 60, mol ratio), taking the formula as $\text{Ca}_2\text{Si}_3\text{O}_8$, it is seen that neutralization would be one quarter by the Ca^{2+} and three quarters by the Si^{4+} . In the general case, these are the *equivalent fractions* of the oxides $X(\text{oxide A})$, $X(\text{oxide B})$, etc. Additionally, however, the tendency for covalency causes the electron donor power of the oxide(-II) ions (atoms) to be further decreased, being affected more by the silicon than by the calcium. With this simple picture, a new factor is introduced, the *basicity moderating parameter*, symbol: $\gamma_A, \gamma_B, \dots$, such that

$$\Lambda = \frac{X(\text{oxide A})}{\gamma_A} + \frac{X(\text{oxide B})}{\gamma_B} + \dots \quad (6)$$

This equation is the fundamental expression of optical basicity.

For a binary oxide, $X(\text{oxide})$ is unity and Λ is simply $1/\gamma_M$, so Eq. (6) becomes

$$\Lambda = X(\text{oxide A})\Lambda(\text{oxide A}) + X(\text{oxide B})\Lambda(\text{oxide B}) + \dots \quad (7)$$

Following this, use is often made of relationships of the type

$$\gamma_A = \frac{X(\text{oxide A})}{\{\Lambda - X(\text{oxide B})/\gamma_B\}} \quad (8)$$

It is important to use Eq. (7) with caution because an isolated binary oxide might behave with a different γ value when present in glass. This happens for P_4O_{10} in the $\text{Na}_2\text{O-P}_2\text{O}_5$ glass system when, initially, its Λ value, 0.48, appears to decrease with addition of Na_2O , so the 1 : 1 glass unexpectedly has the same optical basicity as that of the original phosphorus(V) oxide. Lithium borate glasses behave similarly when the stereochemistry of boron changes from trigonal planar to tetrahedral. For silicate systems, however, this complication seldom arises, so it has been consistently found that γ is 2.100 ± 0.001 for silicon. By Eq. (8), it thus becomes possible to obtain the γ_M values for other metal ions using the spectroscopically obtained Λ values that are available (Table 1). These are substituted into Eq. (6) to calculate Λ of the medium,

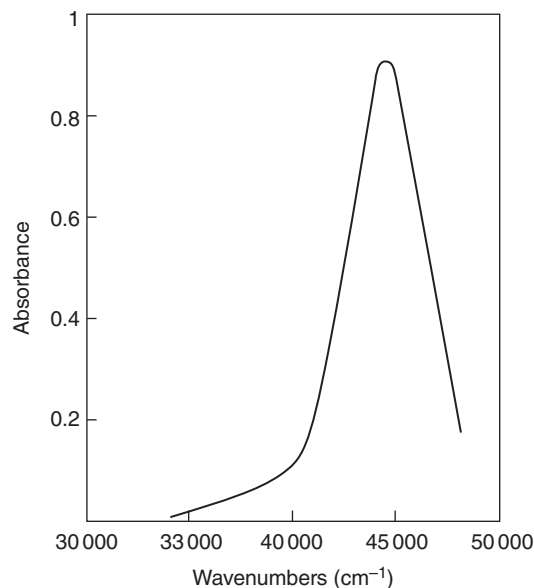


Figure 1 Optical absorption spectrum (in the UV region) of Pb^{2+} probe ion dissolved in sodium borate glass (20 mol % Na_2O). Pathlength: 1.5 mm; Pb^{2+} concentration (nominal): $1.1 \times 10^{-3}\text{ M}$. Note: Increasing wavenumber corresponds to decreasing wavelength, e.g. $30\,000\text{ cm}^{-1} \equiv 333\text{ nm}$ and $50\,000\text{ cm}^{-1} \equiv 200\text{ nm}$.

Table 1 Original (pre-2002) values of γ_M for cations^a and Λ for binary oxides.

Cation	Basicity moderating parameter, γ_M	Optical basicity, $\Lambda(\text{oxide})$
Lithium	1.00	1.00
Sodium	0.87	1.15
Potassium	0.73	1.4
Cesium	0.60	1.7
Calcium	1.00	1.00
Strontium	0.9	1.1
Barium	0.87	1.15
Magnesium	1.28	0.78
Aluminum	1.65	0.60
Silicon	2.10	0.48
Boron	2.35	0.42
Phosphorus	2.5	0.40

^a See Table 3 for post-2002 values.

thereby allowing one to correlate the chemical formula of the glass or slag with its physical and chemical properties [4]. Thus it is possible to predict changes in physical/chemical properties from changes in the chemical formula of the melt.

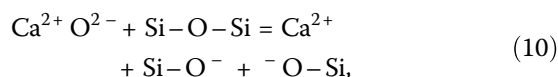
Sometimes it is necessary to consider two important questions: (i) whether the probe ion occupies already existing sites or whether it “misbehaves” and generates its own site and (ii) whether or not the optical basicity changes when the melt transforms to a glass, and vice versa. These two questions are intermingled and have been given careful consideration. As described below, it has gradually become apparent how Pb^{2+} , Tl^+ , and various other probes play a valuable role for investigating glass, especially the chemical bonding and structure.

3 Redox Equilibria in Network Melts

Molten silicates, borates, and others are excellent solvents for redox equilibria many of which have technological application (Chapter 5.6). In extraction metallurgy, for example, it is vital to understand how chemical composition affects the ability of the slag to remove troublesome impurities from the molten metal ([5] and Chapter 7.4). In the case of sulfur that is present in molten iron, this property is measured as the sulfide capacity, C_S , (defined as $(\%S) \times \sqrt{(P_{\text{O}_2}/P_{\text{S}_2})}$, where $\%S$ is the weight % of sulfur in the slag and P_{O_2} and P_{S_2} are the equilibrium partial pressures of O_2 and S_2). Experimental data for silicate and aluminosilicate blast-furnace slags at 1500°C show that the overall reaction expressed by Eq. (2) is related to the slag optical basicity by

$$\log C_S = 12.0\Lambda - 11.9. \quad (9)$$

As a more basic oxide is added, the increase in melt basicity results in the production of further nonbridging oxide(-II). For example, expressing this process as



one represents the transfer of the oxide(-II), initially in an electrovalent environment of CaO , to the silicate melt where it reacts with bridging $\text{Si}-\text{O}-\text{Si}$, thereby producing charged $\text{Si}-\text{O}^-$ units. The bonding between the Ca^{2+} ions and the anionic framework is essentially ionic since a charge of around +1.2 has been estimated to “reside” on the calcium. The balancing negative charge is spread over the oxide(-II) atoms, being more concentrated for the nonbridging oxide(-II)s than for the bridging. The optical basicity idea does not envisage unit negative charge on the nonbridging oxide(-II)s nor a zero charge for bridging oxide(-II)s. The overall charge

increases with increasing optical basicity, which can be thought of in terms of the tendency for the anionic network to provide oxide(-II) “ions” for participation in Eq. (2). Many slag studies have been undertaken by extraction metallurgists for dealing with a wide range of impurities, such as sulfur, phosphorus, water, and so on [5].

Turning now to glassmaking, we note that the presence of redox ion pairs such as the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple often requires careful control of melt composition to stabilize the desired oxidation state [6]. Because of experimental difficulties, investigations have been limited to just a few ion pairs. It has been found that in contrast to the observation made above for sulfur, increasing optical basicity favors the upper oxidation state. To account for this feature, the metal ions are considered initially as being in the isolated, free state, a condition for which Λ is by definition zero. Both ions are unstable to the extent of their ionization energies, that is, the sum of the first + second for Fe^{2+} and the first + second and third for Fe^{3+} . Increasing Λ of the melt corresponds to an increasingly negative environment, and this effects stabilization for both metal ions through chemical bonding in the formation of the $[\text{FeO}_6]$ or some other chromophore. Because of the larger cationic charge for the trivalent ion, however, a greater optical basicity is required for Fe^{3+} . This extra charge can be pictured as being fed through electron delocalization (mainly by π -bonding) from the nonbridging oxide(-II)s generated in Eq. (10). The stabilization of upper oxidation state ions by increasing optical basicity is probably general (except for $\text{Cu}^{2+}/\text{Cu}^+$) and is satisfactorily expressed in terms of two empirical parameters, a and b :

$$\log \left\{ \frac{[\text{lower state}]}{[\text{upper state}]} \right\} = a - b\Lambda. \quad (11)$$

Results for silicate melts at 1400°C and in an air atmosphere are summarized in Table 2.

Table 2 Relationship of redox ratio, R , for ion couples with optical basicity; $R = [\text{lower state}]/[\text{upper state}]$ in silicate melts at 1400°C in air atmosphere.

Ion couple	Equilibrium	$\log R$
$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	$4\text{Fe}^{3+} + 2\text{O}^{2-} = 4\text{Fe}^{2+} + \text{O}_2$	3.2–6.5 Λ
$\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$	$4\text{Cr}^{6+} + 6\text{O}^{2-} = 4\text{Cr}^{3+} + 3\text{O}_2$	8.2–13.7 Λ
$\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$	$4\text{Ce}^{4+} + 2\text{O}^{2-} = 4\text{Ce}^{3+} + \text{O}_2$	5.5–8.3 Λ
$\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$	$2\text{Sn}^{4+} + 2\text{O}^{2-} = 2\text{Sn}^{2+} + \text{O}_2$	0.6–3.6 Λ
$\text{As}^{5+} \rightarrow \text{As}^{3+}$	$2\text{As}^{5+} + 2\text{O}^{2-} = 2\text{As}^{3+} + \text{O}_2$	5.2–8.9 Λ

The optical basicity model is not restricted to glasses and melts but applies equally well to aqueous solutions [7]. Electrode potential data in acidic and basic aqueous solution at 25 °C have provided a means for predicting a and b for several ion pairs for which no directly obtained results (at 1400 °C) are available. By similar means, Λ has been correlated with the tendency for precipitation of the element out of the molten glass, for example, platinum, silver, and lead.

It is of interest that early attempts to create a scale for basicity involved many studies of glasses containing redox ion pairs and correlating their equilibria with glass composition. UV/visible spectrophotometry was often used. With color changes occurring for decreasing basicity, commonly chosen ion pairs and their chromophores were $\text{Cr}^{6+}/\text{Cr}^{3+}$ (yellow owing to $[\text{CrO}_4^{2-}]$)/(green, owing to $3d^3$ $[\text{CrO}_6]$); $\text{Mn}^{3+}/\text{Mn}^{2+}$ (red owing to $3d^4$ $[\text{MnO}_6]$)/very pale pink (owing to spin-forbidden d^5 $[\text{MnO}_6]$); $\text{Ce}^{4+}/\text{Ce}^{3+}$ (orange owing to charge transfer)/colorless (owing to $[\text{Ce}^{3+} 4f^1 \rightarrow 5d$ band in the UV]); and the stereochemical change of Co^{2+} deep blue [tetrahedral CoO_4]/pale pink [octahedral CoO_6].

4 Optical Basicity and Electronic Polarizability

To explore the possibility of a more “fundamental” optical basicity scale, investigation can be made into the relationship between Λ and the oxide(-II) electronic polarizability. The real part, n , of refractive index of glass is a measure of the reduction in the velocity of the photons as they induce oscillating distortions of the electron charge clouds when they pass through (Chapter 6.1). The electronic polarizability, α , expresses the ease of exercising this distortion for the particular cations and anions of the glass. These values are more or less fixed, except for oxide(-II) where $\alpha_{\text{oxide(-II)}}$ varies over a wide range. In a glass the value of $\alpha_{\text{oxide(-II)}}$ is part of the total electronic polarizability, α_{mol} : one obtains it, therefore, by subtracting the total cationic polarizabilities, $\sum \alpha_i$, and dividing by the number of oxide(-II) atoms assumed in the formula of the glass:

$$\alpha_{\text{oxide(-II)}} = \frac{[\alpha_{\text{mol}} - \sum \alpha_i]}{\text{total oxide(-II)}}. \quad (12)$$

Use of the Lorentz–Lorenz relationship

$$\alpha_{\text{mol}} = \left[\frac{3V_m}{4\pi N} \right] \times \left[\frac{(n^2 - 1)}{(n^2 + 2)} \right], \quad (13)$$

allows α_{mol} (in $\text{\AA}^3$) for the glass to be calculated (assuming isotropy) from the refractive index, n (usually the sodium D line), and density, ρ . In Eq. (13) V_m is the molar volume

(formula weight/density) and N is Avogadro’s number. As an example, we take the glass of mole percentage composition 0.33 Na_2O ·0.095 CaO ·57.2 SiO_2 , which has a refractive index of 1.529 and density of 2.652 g/cm^3 . Its arbitrary formula weight in grams is $(33.3 \times 61.98 + 9.5 \times 56.08 + 57.2 \times 60.08)$, and V_m is $6033/2.652 = 2275 \text{ cm}^3$. From Eq. (13), α_{mol} , the polarizability of the glass, is 278.25 $\text{\AA}^3$. We subtract the cationic polarizability of Na^+ , Ca^{2+} , and Si^{4+} , i.e. $\sum \alpha_i = 17.33 \text{ \AA}^3$ (using values of α_M in Table 3), and divide by the number of oxide(-II) atoms assumed in the formula of the glass, i.e. 157.2. The $\alpha_{\text{oxide(-II)}}$ polarizability is therefore $(278.25 - 17.33)/157.2$, i.e. 1.660 $\text{\AA}^3$.

To derive now the sought-after “fundamental” optical basicity scale, the substitution into Eq. (6) is made using the most reliable basicity moderating parameters, namely, of calcium(II) and silicon(IV). Their γ_M values are 1.00 (by definition) and 2.00 (cf. Section 2), respectively. In 2002, published refractivity data (n and ρ) were available for 15 calcium silicate glasses from 39.0 to 57.5 mol % CaO . From these data, values of α_{oxide} are obtained as indicated above, and Eq. (6) gives Λ_{glass} values for each of the glasses. When plotted together with the same data for crystalline SiO_2 and CaO (Figure 2), these data reveal the relationship very close to [8]:

$$\Lambda_{\text{glass}} = \frac{[(3.133\alpha_{\text{oxide(-II)}} - 2.868)^{1/2}]}{1.567} - 0.362. \quad (14)$$

Significantly, unlike the probe-ion method for measuring Λ , this new one is noninvasive and avoids the possible probe-ion misbehavior noted in Section 2.

For many glasses the optical basicity ranges from approximately 0.3 to 0.65, an interval for which Eq. (14) can be simplified to:

$$\Lambda_{\text{glass}} = 0.699\alpha_{\text{oxide(-II)}} - 0.547. \quad (15)$$

In principle, Eqs. (13) and (12) then (14) or (15) allow the optical basicity of a (binary) silicate glass to be calculated from its density and refractive index and the γ_M value to be obtained from Eq. (8). The values derived in this way are listed in Table 3. Mostly they differ only slightly from the earlier probe-ion method; lithium seems the single exception.

5 Chemical Reactions: Changes in Structure and Bonding

For technological reasons, the interaction of SiO_2 with CaO , Na_2O , etc. usually takes place in the lower-melting cullet. The optical basicity of SiO_2 is 0.48, corresponding

Table 3 Electronegativity, x_M , polarizability, α_M , and $\alpha_{\text{oxide(-II)}}$ in binary oxides; basicity moderating parameter, γ_M , also in glasses.

Oxide	x_M	$x_O - x_M$	x_O	% ionicity	α_M ($\text{\AA}^3$)	$\alpha_{\text{oxide(-II)}}$ ($\text{\AA}^3$)	γ_M
Cs ₂ O	0.79	1.49	2.28	80	2.42		0.66
Rb ₂ O	0.82	1.51	2.33	73	1.40		0.70
K ₂ O	0.82	1.56	2.38	66	0.83		0.76
Na ₂ O	0.93	1.65	2.58	54	0.179		0.905
Li ₂ O	0.98	1.91	2.89	45	0.029	1.58	1.23
BaO	0.89	1.86	2.75	74	1.55	3.7	0.75
SrO	0.95	1.91	2.86	59	0.86	3.07	0.95
CaO	1.00	1.97	2.97	58	0.47	2.49	1.000
MgO	1.31	1.92	3.23	34	0.094	1.71	1.10 ^a
La ₂ O ₃	1.10	1.97	3.07	67	1.32		0.85
Y ₂ O ₃	1.22	1.90	3.12	56	0.55	2.47	0.96
Sc ₂ O ₃	1.36	1.88	3.24	50	0.286	2.14	1.11
Al ₂ O ₃	1.61	1.86	3.47	21	0.052	1.46	1.65 ^a
SiO ₂	1.90	1.67	3.57	22	0.0165	1.41	2.10 ^a
B ₂ O ₃	2.04	1.66	3.70	18	0.003	1.39	2.47 ^b
P ₂ O ₅	2.19	1.45	3.64	17	0.00	1.33	2.1 ^c

^a For fourfold coordination; for sixfold, $\gamma_{\text{Mg}} = 1.65$, $\gamma_{\text{Al}} = 2.48$, $\gamma_{\text{Si}} = 3.15$.
^b For threefold coordination; for fourfold, in borate glasses, $\gamma_{\text{B}} = 4.2$.
^c Varies in phosphate glasses.

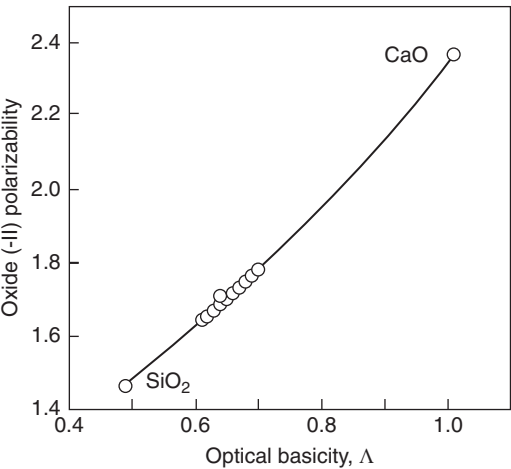


Figure 2 Plot of oxide(-II) polarizability, $\alpha_{\text{oxide(-II)}}$, versus optical basicity of calcium silicate glasses, 39–57.5 mol % CaO (Λ range, 0.60–0.69). Data for SiO₂ and CaO at the extremes ($\Lambda = 0.476$ and 1.000, respectively). Ignoring the data point for CaO, the line fits Eq. (14).

to a Λ -difference between SiO₂ and these bases usually of well over 0.5. Similar differences are evident for borate, phosphate, and the glasses of certain other oxides. For many of these glass systems (though not for silicates),

however, the increase in the experimental Λ varies irregularly with glass composition. This occurs for borate glasses where γ_{B} , which is 2.47 for both vitreous and crystalline B₂O₃, deviates markedly from Eqs. (6) and (7) upon addition of alkali to the glass. This is observed in the UV spectra of Pb²⁺ and Tl⁺ probe ions and also with the far-infrared frequencies of “rattling” Na⁺ ions [9]. The most obvious cause of this effect is the well-known structural change of boron from trigonal planar to tetrahedral coordination ([1], Chapter 7.6). One of the most important results of this change is the elimination of the π -component from the bonding of oxide(-II)s that are attached to the four-coordinated boron atoms. The π -bonding in glass is normally important for the delocalization of electronic charge and for the benefit that this undoubtedly has for reactions occurring in the glass or melt. Thus, the newly formed tetrahedral BO₄[−] units become “stops” embedded in the overall electron delocalization associated with the glass structure.

An interesting feature of chemical bonding in inorganic compounds is that the σ -component serves to transfer negative charge from the donor to the acceptor atom. Normally this is supplemented by some degree of π -bonding, which allows further donation of negative charge. In addition, π -bonding can provide “back-coordination” where some of the negative charge spills back to

the donor atom. This scheme of bonding is recognized as a means for preventing the buildup of positive or negative charge in a molecule and is known as the (Pauling) *electroneutrality principle*. In the case of the BO_4^- units, we have been discussing that the absence of π -bonding means that any back-coordination cannot occur; there is the possibility that in the BO_4^- unit the negative charge resides mainly on the boron atom. Accordingly the basicity moderating parameter, γ_B , of the boron atom is appreciably higher than for trigonal planar boron. This idea of an increase in γ_B is supported by an analysis of the refractivity data for alkali borate glass systems where calculated values of $\alpha_{\text{oxide(-II)}}$ are substituted into Eq. (14). The results show how Λ for each glass increases only very slowly for initial additions of alkali oxide, whereas for lithium oxide there is a *decrease* in Λ up to a Li_2O content of approximately 25 mol %. It appears that the γ_B value for tetrahedral boron is counter-effective to the increasing basicity of the relatively feeble alkali oxide. When Eq. (8) is adapted to accommodate also the (unknown) γ_B value for tetrahedral boron, calculations reveal that the γ_B value for tetrahedral boron is 4.7 [10] on the slightly false assumption that exactly two are generated by each added oxide(-II) atom.

At this point, there is an important question. Does the *chemical behavior* of a series of glasses, such as the stabilization of upper/lower oxidation states of metal ions (Section 3), follow the same trend as the calculated optical basicity, for example, in the case of borate glasses when the calculation assumes γ_B equal to 2.47 for threefold coordinated boron and 4.7 for fourfold. Experimental data for the redox ion pairs $\text{Cr}^{6+}/\text{Cr}^{3+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ indicate that such a parallel does indeed exist. For these ion pairs there is the usual trend of the upper oxidation state being favored by increasing alkali oxide content, but this trend is very slight for initial additions of oxide to boric oxide, and, dramatically, for Li_2O , the trend is the *reverse* for both ion pairs. It is only after approximately 25 mol % Li_2O that the more usual effect of upper oxidation state stabilization occurs. This startling trend almost exactly parallels the trend in the calculated optical basicity, making the result highly significant. It illustrates how *deviations in predicted optical basicity* are paralleled by corresponding *deviations in chemical behavior*. Looked at in another way, deviations in the properties of a glass system with composition, often described as “anomalous behavior,” can be understood, at least partially, in terms of a chemical bonding analysis of the type described here. It also emphasizes the importance of π -bonding in the glass network and the consequences if it is lost.

Another aspect concerning the combination of optical basicity and chemical bonding is the success for identifying the ionic/covalent nature of the sites

provided by a glass as metal ions travel through. Studies of phosphate glasses and melts and especially of borate glasses indicate that sites of higher rather than of lower optical basicity are favored by mobile metal ions (and vice versa) [9]. For example, subjecting a 35 mol% Na_2O sodium borate glass, coated with a thallium–Hg amalgam and floating on mercury, to an electric field results in driving Tl^+ ions into the glass [6]. After sub-surface cleaning with an ion beam, the UV spectrum of the Tl^+ ions indicates the existence of sites of optical basicity equal to 0.66–0.67, which is much greater than expected for this glass. The assistance to ionic mobility might be anticipated for sites where the interaction with oxide(-II) is more covalent, as signaled by the large Λ , since the influence of large lattice energies is bound to be less important. Similar experiments using lead rather than thallium show little movement of Pb^{2+} ions into the glass. Instead, O^{2-} ions migrate to the lead electrode, with formation of PbO , while Na^+ ions are converted to sodium at the mercury electrode. This leaves a volume of the original sodium borate glass that is devoid of Na_2O : it has become a volume of vitreous boric oxide. The mechanism proposed for this reversible reaction involves a “handing over” of oxide(-II) ions between threefold and fourfold coordinated boron atoms [11].

For the interaction of silicates with phosphates, borates, etc., or even with other silicates, there is sometimes the problem of deciding which “salt” is the acid and which is the base. For example, when considering the equilibrium



does twice the amount of alkali oxide in Na_2SiO_3 on the left-hand side compensate for the stronger basicity of K_2O in $\text{K}_2\text{Si}_2\text{O}_5$? Calculations with Eq. (6) show that Λ is 0.65 for $\text{K}_2\text{Si}_2\text{O}_5$ and 0.69 for Na_2SiO_3 , indicating that Na_2SiO_3 is the base. Furthermore, on the right-hand side, Λ is 0.76 for K_2SiO_3 and 0.61 for $\text{Na}_2\text{Si}_2\text{O}_5$, so the *optical basicity differences* are 0.04 and 0.15 for the left- and right-hand sides, respectively. It follows that Eq. (16) represents an acid–base neutralization and should proceed from right to left, which indeed is found to be the case. This consideration of Eq. (16) illustrates how, within a material, chemical bonding results in an uneven distribution of electrical charge and how optical basicity reflects the extent of the negative charge borne by the anionic moiety, presumably on its surface. Thus, when two materials of different Λ are in contact, there exists a chemical driving force that, ideally, is proportional to the optical basicity difference [12]. There are of course many factors influencing reactions of this type, for example, high lattice energy. Nevertheless, examination of sub-solidus compatibility diagrams (as summarized in the

American Ceramic Society's *Phase diagrams for ceramists*) does indicate many instances supporting the idea that optical basicity is an important factor.

The involvement of Λ in the acid–base neutralization for solids discussed above suggests that there might be a similar situation for aqueous conditions through the existence of a relationship with Brønsted acidity. This idea has been tested with suitable sets of pK values for appropriate parent acids, for example, phosphoric acids. In addition to orthophosphoric acid, H_3PO_4 , phosphorus(V) forms several condensed oxyacids containing both bridging and non-bridging oxide(-II)s. Equation (6) gives Λ for each conjugate base (γ_M is set arbitrarily at unity), and one can plot these values against the pK (conjugate acid) values of the various phosphate (and other) species. A roughly linear relationship is obtained, which, moreover, includes the points for water, namely, the bases H_2O and OH^- [4].

6 High and Low Optical–Basicity Materials

It is seen from the periodic table that the nearest neighbor to oxide(-II), with its outer $2s^2 2p^6$ configuration, are fluoride(-I) with the same configuration and sulfide(-II) with the configuration $3s^2 3p^6$. To what extent does the optical basicity model extend to the chemistry of these adjacent elements?

In view of the extra unit nuclear charge, fluoride systems (with no other anion) might be imagined to have optical basicities that are one half of the corresponding oxide systems. It is possible that this situation is equivalent to “one electron worth” of screening in the case of oxide(-II). Probe-ion studies made with Pb^{2+} for molten alkali fluorides remarkably support this idea. Further support comes from polarizability results for crystalline binary fluorides and also complex compounds such as alkali fluoroborates, fluorosilicates, and fluoroaluminates. These results mean that it is possible to use Eq. (6) for calculating the optical basicity of a fluoride glass, but with the condition that the γ_M values are double those for the corresponding oxides, alternatively, by using Eq. (7), but with the oxide Λ halved. It is apparent that with $\Lambda(\text{fluoride}) = \frac{1}{2}\Lambda(\text{oxide})$, some fluoride materials have very low optical basicities, for example, Λ is 0.23 for crystalline $\text{Na}[\text{BF}_4]$ and is 0.35 for the glass $0.100 \text{ MgF}_2 \cdot 0.283 \text{ CaF}_2 \cdot 0.231 \text{ SrF}_2 \cdot 0.386 \text{ AlF}_3$. Mixed fluoride–oxide melts and glasses have been prepared and their refractivity Λ values discussed comparatively with all-oxide glasses [13, 14]. In these media the Pb^{2+} probe ion shows that it is responding to a single, mixed oxide–fluoride environment rather than to two distinct environments.

Sulfide(-II) systems are at the other extreme of optical basicity. From the point of view of chemical bonding, some are semiconductors and are close to electron itineracy, for example, mercury(II) sulfide with a band gap $E_g = 2.10 \text{ eV}$. Studies of optical basicity for semiconductors present difficulties, but in recent years various investigations have been undertaken on sulfur, selenium, and tellurium semiconductor-type materials (e.g. [15]). For crystalline ZnS , a more amenable semiconductor, Pb^{2+} , has its $^1\text{S}_0 \rightarrow ^3\text{P}_1$ frequency at $20\,400 \text{ cm}^{-1}$ in zinc blende and at $19\,700 \text{ cm}^{-1}$ in wurtzite. These yield $\Lambda = 1.30$ and 1.32 respectively, that is, a significantly greater basicity compared with $\Lambda = 0.91$ for ZnO . Trends for MgS , CaS , SrS , and BaS in electronegativity and polarizability fit into the same pattern as for fluorides and oxides.

Perhaps it is surprising that the optical basicity of water itself has been subjected to so little study. It will be recalled that in the development of the nephelauxetic effect (Section 2), Jørgensen set h for H_2O as unity. One of the reasons for this assignment was the consistency of d–d spectral data for $[\text{M}(\text{H}_2\text{O})_n]^{z+}$ chromophores (n , normally six), and with $h = 1.00$ and $\Lambda = 0.39$ for H_2O . However, it appears that when the constricted conditions of the coordination sphere are removed, Λ for the free H_2O molecule rises to 0.51. Further work in this area is called for.

It is of interest that “less related” anionic systems have been investigated, for example, molten chlorides, where probe ions indicate the possibility of establishing a chloride optical basicity scale [2]. Acid–base titrations, for example, have been performed with molten AlCl_3 .

7 Optical Basicity and Electronegativity

It is not surprising that there should be a link between electronegativity, x , and optical basicity since both schemes are concerned with unequal sharing of electronic charge in chemical bonding. In terms of the basicity moderating parameter, γ_M , and the Pauling-type electronegativity, x_M , it has long been established [1] that

$$\gamma_M = \frac{(4x_M - 1)}{3}. \quad (17)$$

with the condition that this relationship is restricted mainly to the M cations having the outer s^2p^6 configuration, thereby excluding most transition metal ions. This condition also applies for Eq. (18).

Although for binary oxides x_O is usually assigned a value of around 3.5, closer inspection shows that this value refers only to the “covalent” oxides (see Table 3). However, with increasing ionicity in the metal–oxide

(-II) bonding, there is a marked decrease in x_O . The effect is shown in Figure 3 where the points (unlabeled for clarity) are for the oxides shown in Table 3. Most lie close to the relationship [12]

$$x_O = \frac{4.1 - 0.86}{(x_M - 0.25)}. \quad (18)$$

The reason for this decrease in x_O is that the increasingly negative charge on the covalently bound oxide (-II) atom renders it reluctant to acquire further negative charge. It becomes unstable with a tendency to lose an electron and to form the peroxide, $(O-O)^{2-}$, or superoxide, $(O-O)^-$, ion. Generally, the electronegativities that are assigned to the elements, in a particular oxidation state, are taken as “fixed,” but the oxide(-II) species stands out as a gross exception. Indeed, the trend shown by Figure 3 is an *abnormality* compared with the other elements in the periodic table. It might be argued that it is this feature that allows optical basicity to operate in a significant way.

The non-fixed character of x_O has a profound effect on the use of electronegativity as an indicator for trends in ionicity or covalency. In general, it is the electronegativity difference that denotes such a trend, as in the series from iodide to bromide to chloride. However, this scheme has limited application for oxides. As seen in Table 3, the electronegativity difference between Na_2O and SiO_2 hardly exists, $x_O - x_{Na} = 1.65$ and $x_O - x_{Si} = 1.67$, even though Na_2O is ionic, whereas SiO_2 is covalent; similar cases are ionic BaO and amphoteric Al_2O_3 where for both, $x_O - x_M$ is 1.86. Among others, these considerations show that for binary oxides of general formula M_aO_b , it is

the decreasing value of x_O that signals increasing ionicity in the metal–oxide(-II) bonding. The value of $x_O - x_M$ for each binary oxide in Table 3 is obtained from its enthalpy of formation, Q (in electron volts, that is, $-\Delta H_f^\circ/96.48$, with ΔH_f° in kJ/mol) divided by the “number of bonds,” b (two for CaO , four for SiO_2 , etc.), where Q requires the addition of 1.13 eV per oxygen because of the double bond in the O_2 molecule. On the Pauling scale, the electronegativity difference, $x_O - x_M$, is given as

$$x_O - x_M = \left[\frac{(Q + 1.13b)}{2b} \right]^{1/2}. \quad (19)$$

Assuming x_M to be invariant, then one obtains x_O by addition (Table 3). The relationship of for example (17–19) leads to the following expression linking the heat of formation of a binary oxide, M_aO_b , with its optical basicity [16]:

$$\frac{Q}{b} = 2 \left[\frac{2.85 - 1.16\Lambda(M_aO_b) - 0.75}{\Lambda(M_aO_b)} \right]^2. \quad (20)$$

This relationship has been applied to silicates and aluminosilicates. For example, $CaO \cdot Al_2O_3 \cdot 2 SiO_2$ requires use of Eq. (20) for each of the three constituent oxides, followed by addition of the relevant Q values to obtain the total Q for the compound. Results have shown that with some refinements to Na_2O and K_2O (see Figure 3), there is a convincing correlation of Q with the optical basicity of the compound. Since Λ is related to chemical constitution through Eq. (6), it is apparent that optical basicity offers a method for calculating the heat of formation of a silicate or an aluminosilicates from its chemical constitution [16].

It is surprising that in the past, with some exceptions, the chemical bonding aspects of glass have tended to be ignored or considered only at a fairly elementary level. Usually the approach is in terms of valence-bond theory with the depiction of electron pairs. Alternatively it is in terms of band theory where electrons are “accommodated” in energy bands. How does the concept of optical basicity connect with these approaches? As explained in Section 2, it is already apparent that optical basicity itself is derived from a molecular orbital approach in exploiting orbital expansion parameters. This connection has allowed calculations for binary oxides (using ionization energies for isoelectronic sets of free ions) that provide estimates of charge-cloud sharing and hence of the ionicity of M^{Z+} (see Table 3). Although they incorporate arbitrary assumptions (as do other atomic/ionic parameters, e.g. ionic radii), nevertheless, these data are useful for comparative purposes. In effect, optical basicity serves to indicate ranking in the ionic/covalent character of the chemical bonding in a similar way that electronegativity difference does for simple non-oxide(-II) compounds.

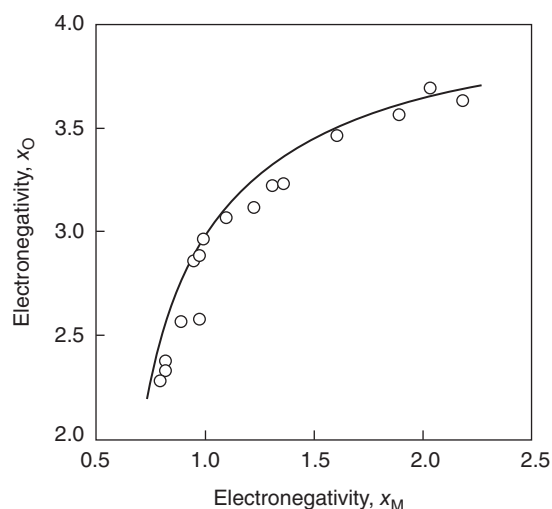


Figure 3 Plot of oxide(-II) electronegativity, x_O , in binary oxides M_aO_b , against electronegativity, x_M (see Table 3). Points at bottom left-hand area are for “ionic” oxides; those at the top are for “covalent” oxides.

For a glass or melt, it is the uneven spread of electron density over the electronic surface of the “molecules” (for want of a better word) that is responsible for many of its properties, for example, as a reaction medium for redox equilibria.

Historically, a related point of interest concerns the Lorentz–Lorenz relationship, Eq. (13), and how the molecular polarizability, α_{mol} , replaced the molar refractivity R_m (in cm^3) in the Clausius–Mossotti expression:

$$R_m = \frac{V_m(\kappa - 1)}{(\kappa + 2)}, \quad (21)$$

where V_m remained the molar volume, in cm^3 , but, κ , the dielectric constant, became n^2 (Maxwell, strictly at infinite wavelength). When Eq. (21) is written as

$$\frac{R_m}{V_m} = \frac{1 - 3}{(\kappa + 2)}, \quad (22)$$

it is seen that as the value of V_m decreases and approaches R_m (effected by compression or chemical substitution of a metal oxide “bronze,” for example), κ approaches infinity. This condition corresponds to a *polarization catastrophe* and the onset of metallic bonding. In terms of simple band theory, the energy gap (or band gap), E_g , becomes zero as the valence band and conduction band merge into each other. Indeed, the plot of E_g for oxides reveals a close proximity to the empirical expression [17]:

$$E_g = 20 \left(\frac{1 - R_m}{V_m} \right)^2, \quad (23)$$

which implies again that E_g is zero when $V_m = R_m$.

It should be noted that the quantities of both R_m and $\alpha_{\text{oxide(-II)}}$, together with Eq. (23), have, all three, optical basicity as their common link. There are many occasions when chemical bonding is regarded in terms of a sliding scale from covalent to ionic (for example, see Table 3). However, this description is often inadequate, especially when so many materials are viewed in terms of dielectrics, semiconductors, and metals (or insulators, semiconductors, and conductors). Such inadequacies confront glass science. As far as oxide glasses are concerned, Figure 4 is relevant in providing a small selection of binary oxides in an attempt to illustrate these aspects of bonding. The horizontal scale denotes covalent to ionic (through Pauling-type electronegativity, x_O), and in addition, progressing upward from that scale, there is increasing tendency for electron itineracy. The latter feature might be described as the “metallic component” of bonding, increasing with decreasing E_g and with the upper limit (the metallic regime) at E_g equal to zero. To indicate

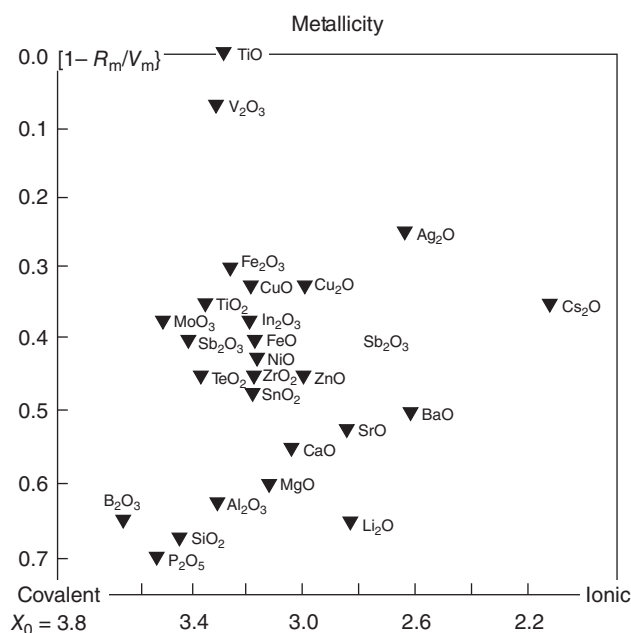


Figure 4 Schematic bonding chart for binary oxides (abbreviated for clarity): covalency to the left-hand side and ionicity to the right; height indicates closeness to nonmetal-to-metal transition.

the unifying approach provided by optical basicity for these types of chemical bonding, the alternative to E_g , namely, $(1 - R_m/V_m)$, is taken as the vertical scale (see above). The diagram implies that increasing electron itineracy can be a feature regardless of the ionic/covalent nature of the bonding of the oxide. A more complete diagram is discussed by Edwards et al. who also considered the onset of metallicity generally [17].

8 Perspectives

The Lewis idea of chemical bonding, where a base is a donor of electronic charge and an acid an acceptor, is well suited for many inorganic oxide(-II) materials and has been implicit in the present review. Under chemical conditions, the electronic state of oxide(-II) has a flexibility that is greater than for any other element. This accounts for its wide range of electronegativity, x_O , of its electronic polarizability, $\alpha_{\text{oxide(-II)}}$, and of its ability to donate charge when acting as a Lewis base. All of these features are incorporated into the optical basicity model.

At the heart of optical basicity is the existence of a hypothetical array of oxide(-II), O^{2-} , ions. These are influenced by the constituent cations, Ca^{2+} , Si^{4+} , ..., according to the extent that they balance the overall negative charge, that is, according to their equivalent fractions, X_{Ca} , X_{Si} , In addition, there is unequal sharing

of the charge density in the chemical bonding. The combination of the two effects determines the electronic state of the oxide(-II) in terms of its power to react as a Lewis base (for example, in breaking up the silicate network; see Eq. 10) and in terms of its electron donor power (for example, in its coordination with probe cations). The overall effect is expressed, for the cation, as its basicity moderating parameter, $\gamma_{\text{Ca}}, \gamma_{\text{Si}} \dots$, and for the compound as the optical basicity, Λ , according to Eq. (6).

This model is set in the context of well-established chemical theory and incorporates a background of molecular orbital theory and orbital expansion phenomena. The effective functioning of optical basicity and its universal application, which also includes catalysis and geochemistry, are because of this “pedigree.” Inorganic oxidic materials, from network glasses and melts on the one hand to aqueous solutions on the other, are amenable to the optical basicity approach [6, 7, 18].

Practically, optical basicity started with probe ions (Pb^{2+} , Tl^+) and the quantitative treatment of the orbital expansion effect in their electronic spectra, mainly in the UV/visible (optical) region of the spectrum. The optical basicity scale derived from these data correlates well with the chemistry and physics of the media. This provides a means for predicting the trends in properties for a series of glasses using Λ values calculated from chemical constitution with Eq. (6). Noninvasive methods for measuring optical basicity, such as the use of oxide(-II)-1s energies [19], oxide(-II) polarizabilities ($\alpha_{\text{oxide(-II)}}$; see Section 4), or cation rattling frequencies in the far-infrared region [9], have extended the usefulness of optical basicity. They help to provide much needed insights into the nature of chemical bonding in glass and for the interaction with hosted cations, whether static or field driven.

Generally, the optical basicity model implies two important facts about the structure and bonding of glass that, at the present, are often overlooked. First is the existence of electron delocalization (analogous with aromaticity in organic chemistry, though perhaps to a lesser degree), and second is the absence of whole electron charges, for example, on nonbridging oxygen atoms. By implication, the overall existence of some degree of π -bonding must be assumed. For borate systems, partial loss of this feature, accompanying the switch from threefold to fourfold coordination, accounts for some anomalous behavior. Deeper study into these features, not only for borate but for phosphate, germanate, and other glasses, will lead to a better understanding of the mechanism for field-driven ion transport, including movement of O^{2-} ions through the glass [6, 11]. Acquiring a better understanding of chemical bonding, especially the onset of metallization, is vital for the development of glass science, so glass continues to expand its role as a future material [17].

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5.8

The Glass Electrode and Electrode Properties of Glasses

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*Nothing tends to the advancement of knowledge as
the application of a new instrument*

Sir Humphry Davy (1778–1829)

1 Introduction

As indicated by the Latin term *acidus* (from *aceo*, to be sour, deriving from *acer*, sharp, piercing), the notion of acidity has very long been familiar even though it was understood poorly. As a reminiscence of the atomic theory of Democritus (ca 470–380), the chemist Nicolas Lémery (1645–1715) [1] still assigned acidity to tiny particles when he wrote that “the acidity of a liquor consists in sharp salt particles, which keep moving.” As evidences, he explained, were the tingling on the tongue caused by acids or the fact that “not only all acid salts crystallize as spikes but all dissolutions of different matters caused by acid liquors are taking the same figure upon crystallization.” Differences in acidity then simply resulted from differences in the size and sharpness of these particles.

The concept of *base* is much more recent. Because of the close association traditionally made between acids and salts, it was heuristically propounded by another famed chemist, Guillaume-François Rouelle (1703–1770), to describe “the substance that serves as a basis” (*base*, in French) to an acid for the precipitation of a salt [2]. In spite of the tremendous progress that followed Lavoisier’s chemical revolution at the end of the eighteenth century, however, a precise definition of relative acidity–basicity along with ways to measure it remained lacking. It was

in 1909 that work made in Copenhagen at the Carlsberg Laboratory on the effect of acidity on proteins led S.P.L. Sørensen (1868–1939) to define pH, for *pondus hydrogenii* (hydrogen weight), as the cologarithm of the hydrogen ion concentration in an aqueous solution [3]. Thanks to progress made in the thermodynamics of solutions, Sørensen redefined in 1924 his fundamental concept of pH in terms of the *activity* of the hydrogen ion [4]. From the equilibrium dissociation of water into H⁺ and OH[−] ions, it then followed that a solution is acidic or basic depending on whether its pH is lower or higher than 7, respectively.

The usefulness of these definitions would have been very limited, however, had not means to measure hydrogen activity been devised. It is in this respect that glass had a considerable impact by having made measurements possible as soon as the pH concept was defined. The *glass electrode*, whose centenary was commemorated in 2009 [5], was in effect a fundamental invention. Its working principle is rather simple: it is the electromotive force (emf) produced when cations are exchanged between the glass surface and the investigated solution. But the phenomena actually involved are much more complicated than long thought, so a theoretical understanding of the glass electrode has long been lagging behind its various applications. Actually, the possibility to vary at will the composition of glass electrodes was a critical factor in their successful design. These could thus be customized to work over specific pH and temperature ranges and, in addition, used to measure the activity of other singly charged cations such as the alkalis, Ag⁺, or even NH₄⁺, illustrating how a successful concept can then be applied to unsuspected fields.

To describe these features, the various kinds of glass electrodes and their uses will be first presented. We will then show how the determining influence of chemical composition on the properties of the glass

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electrode may be in turn used to investigate the structural role of cations in glass. As made in particular by the School of Nikolskii–Schultz at Leningrad/St. Petersburg (SPb) University, the successive steps to understand theoretically the glass electrode will be reviewed finally.

2 Types and Properties of Glass Electrodes

2.1 The Glass Electrode

At the origin of the glass electrode were the bioelectric experiments made by the physiologist Max Cremer (1865–1935). Knowing that glass possesses electroconductivity, he investigated the emf of a cell made up of a glass membrane connecting two aqueous solutions and found that it varies with the difference in their acidity/basicity [6]. But it was the electrochemist F. Haber (1868–1934), of ammonia synthesis fame, and his PhD student Z. Klemensiewicz who shortly afterward took advantage of the phenomenon to design the *glass electrode* as an instrument for determining acid–base titration curves that had the great advantage over the Pt|H₂ electrode in that it was insensitive to redox potential and devoid of the possible catalytic action of Pt on the solution [7].

Both Cremer and Haber worked with an industrial glass whose electrical resistivity was quite high. To reduce the resistance of electrode, glass membranes were thus made very thin, even after Mac-Innes and Dole had optimized their sensitivity with a 22% Na₂O · 6% CaO · 72% SiO₂ glass [8]. Such fragile and not very sensitive glass electrodes remained used only for laboratory research until they found in the late 1930s the innumerable applications still known today as a result of further glass optimization to make the bulb sturdier, of electronic amplification of the weak emf signal, and of the design of portable instruments fully incorporating the electronics along with both glass and reference electrodes as made by the then UCLA faculty George Beckman (1900–2004) with his instrument, which he named *pH meter*.

A glass electrode is made of two different glasses, one for the insulating tube and the other for a thin membrane that is most often blown as a bulb (Figure 1a). To restrict the pH measurement to the bulb area, the former has a resistivity from five to seven orders of magnitude higher than that of the bulb, with typical values of 10¹⁶ and 10¹⁰ Ω m, respectively [9]. Thanks to the limitless shapability of glass, the membranes may be easily formed to the requirements of particular applications, e.g. flat sensors for surface measurements (on skin or paper) or in small volumes of solutions or as a spear for measurements in soil, meat, etc. To perform the

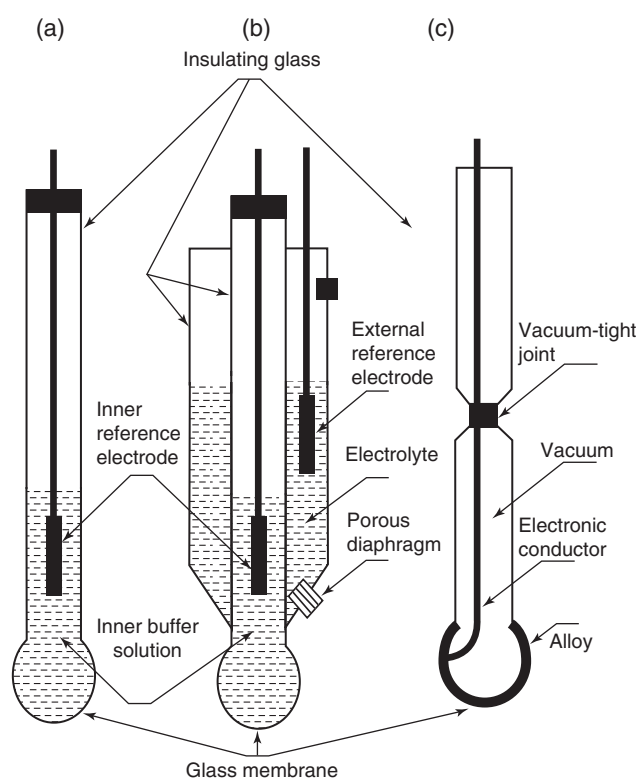


Figure 1 Three kinds of glass electrode design for pH and pM measurements. (a) “Classic.” (b) Combined. (c) With a reversible alloy-based solid internal contact.

measurements a glass electrode requires an external reference electrode. A typical modern pH probe thus is a combination electrode where the HCl solution filling the tube ensures the electrical contact with the glass membrane and encloses an Ag/AgCl reference electrode (Figure 1b).

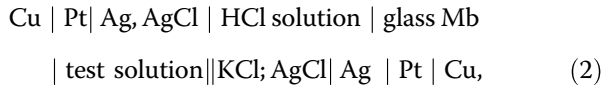
2.2 pH Measurements

In aqueous solutions all ions have a water solvation shell, so the H⁺ ion is just a convenient fiction with which a variety of more complex species, such as the hydroxonium ions (H₃O⁺), are accounted for thanks to the fact that the chemical potential of H⁺ is by definition identical in all such species for systems in internal thermodynamic equilibrium (e.g. [10]). In pH determinations, the H⁺ concentration is expressed in moles of solute per volume of solution (mol/dm³). Following IUPAC recommendations (2000–2002), we will then define pH as

$$\text{pH} = -\text{p}a_{\text{H}} = -\log \left(\frac{m_{\text{H}}\gamma_{\text{H}}}{m^{\circ}} \right), \quad (1)$$

where m is the concentration expressed in molalities (mol/kg), γ_{H} is the activity coefficient of H⁺ ions and $m^{\circ} = 1 \text{ mol/kg}$.

For measurements with a glass electrode, a commonly used galvanic cell is



where $\parallel$ indicates a diffusive barrier. The symmetry of the cell aims at canceling out any potential created at interfaces and, thus, at ensuring that the measured emf only results from the contrast between the test and HCl reference solutions. Operationally, an important parameter is the pH interval where the Nernst equation is valid, namely,

$$E = E^0 + \frac{2.3RT}{F \log a_{\text{H}}} = E^0 - \frac{2.3RT}{F \text{pH}}, \quad (3)$$

where E is the emf of the cell (2) minus the potential of the reference electrode (usually immersed in a 3.5 mol/dm³ KCl solution), E^0 is the standard potential at $a_{\text{H}} = 1$ (or pH = 0), R is the gas constant, T is the absolute temperature, and F is Faraday's number. The value of E^0 includes the diffusion potential at the boundary of the two solutions (which may be eliminated by appropriate means) and the potential at the inner side of the glass membrane, which is not constant but depends on temperature, on the inner solution composition, and on changes in the glass surface induced by the solution.

In view of this complexity, a glass electrode cell is calibrated by means of standard pH buffer solutions before measurements are made. Graphically its pH response in a Nernstian E -pH plot is a straight line whose slope can be considered constant over a definite pH range (Figure 2). The width of this Nernstian range depends on temperature, composition of the electrode glass, and nature and concentration of the acid and singly charged

cations in solution. At high pH, the observed positive deviations from linearity (i.e. the so-called *alkaline errors*) are caused by interferences between H^+ and alkali cations. At low pH, *acid errors* represent deviations from linearity toward negative E values that are due not only to the electrode response itself but also to interferences caused by high anion concentrations.

The membranes of modern pH glass electrodes are produced from lithium silicate glasses to which other oxides are added. As a result of complex optimization, their compositions typically fall in the ranges (in mol %) 21–33 $\text{Li}_2\text{O} \cdot 1\text{--}4 \text{ Cs}_2\text{O} \cdot 3\text{--}5 \text{ La}_2\text{O}_3$ [or Nd_2O_3 , Er_2O_3] $\cdot 1\text{--}4 \text{ CaO}$ [or BaO], where the complement to 100% is SiO_2 . Lithium silicates constitute the base glass because of their high chemical durability and relatively wide region of pH response. Addition of alkaline earth oxides CaO (or BaO) somewhat extends this region toward high pH values, whereas rare earth oxides do so toward low pHs and in addition increase the chemical durability of electrodes with respect to acidic and alkaline solutions. The average values of these oxide concentrations characterize the so-called *universal* glass electrode. These electrodes may be used for general applications at temperatures near ambient showing the Nernstian linear response in a 0–13 pH range in electrolyte solutions with M^+ concentration of 0.1 mol/dm³. Glasses with lower Li_2O concentrations can work at higher pH and higher concentration of interfering alkali ions in solution. Although they are working well at higher temperatures, their high resistance prevents them from being used near ambient. On the contrary, lower working temperatures can be achieved with higher Li_2O concentrations, but the range of linear response then becomes shorter.

2.3 pM Measurements

As made for the H^+ ion, it was early observed that glass electrodes of appropriate compositions are also reacting to concentration changes of other singly charged cations. In analogy with pH, pM scales for the activities of these cations have thus been defined as

$$\text{pM} = -\log a_{\text{M}}. \quad (4)$$

As made of sodium or lithium silicate glasses containing considerable concentration of Al_2O_3 and some B_2O_3 [5], these electrodes show a reversible response to various cations, mainly Na^+ but also K^+ , NH_4^+ , Li^+ , Ag^+ . In the subacid, neutral, and alkaline solutions containing only one of the specified cations, they show almost Nernstian M^+ response for concentrations ranging from saturation to about 10^{-4} mol/dm³. In the presence of other cations, this interval is shorter. They are less common used than pH glass electrode but are nonetheless rather widespread.

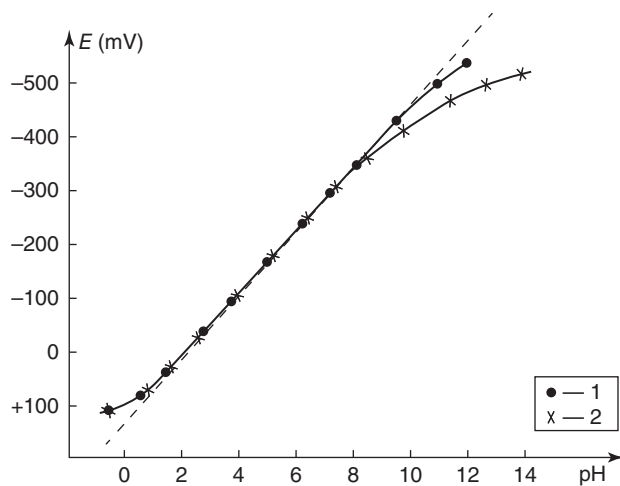
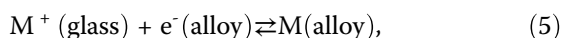


Figure 2 Extent of linearity of the E -pH relationship of a 22 mol % Na_2O silicate glass electrode in solutions: 1 – $c_{\text{Na}} = 0.1$ mol/dm³; 2 – $c_{\text{Na}} = 3$ mol/dm³.

2.4 High-Temperature Glass Electrodes

Glass electrodes with a solid internal contact have been developed to extend the temperature range of measurements up to 200 °C. The difficulty to be overcome was that when Pt, Au, Ag, Cr, Al, or even Hg is used for connections with the glass membrane, the transition from the ionic conductivity of the glass membrane to the electronic conductivity of the contact metal is not reversible. This results in troublesome potentials that may originate from impurities in the contacting metals and fast potential drift. The principles to be fulfilled for overcoming the problem were formulated by Nikolskii [11]: (i) the electrode process occurring at the boundary between an ionic conducting membrane and an electronically conducting contact must of course be itself reversible; (ii) the exchange current of the process must be sufficiently large compared with the current flowing through the system under measurement; (iii) any side process must be prevented at the boundary.

These requirements are satisfied with the metal solid contact invented at Leningrad/St. Petersburg University [5, 12], which consists of a thin layer of an alkali metal alloy evenly spread over the inner surface of a glass membrane. Alloys such as LiIn, LiSn, NaSn, or KPb are formed with the same alkali as present in the glass and the electrode is sealed under vacuum to prevent the alkali from reacting with water vapor. These alloys are electronic conductors in which metal ions are diffusing. Exchange of alkali M^+ ions on the alloy/glass interface takes place according to the reaction



which establishes electrochemical equilibrium and governs the electrical potential at this interface. Because of mutual saturation of the phases, the electrode potential does not depend on the volume of the phases and, thus, to within large limit, on the gross composition of the alloy. In this way potentials are highly reproducible, and E^0 values can be so stable as permitting in some instances to use factory calibrations. An additional advantage is a wide working temperature range, which, for instance, allows these glass electrodes to be sterilized at 150 °C with water steam.

2.5 Glass Electrodes for Redox Measurements

For performing redox measurements other important glass electrodes were elaborated by Pisarevskii et al. in the 1960s [5, 12] on a different basis since the electronic conductivity and activity of electrons relies here on the variable valence states of $Fe^{3+,2+}$ and $Ti^{4+,3+}$. With the compositions (mol %) 10 $Li_2O \cdot 5 Na_2O \cdot 18 Fe_2O_3 \cdot 67 SiO_2$ (type I glass, synthesis under reducing conditions) and 10 $Na_2O \cdot 5 K_2O \cdot 29 TiO_2 \cdot 5 Ti_2O_3 \cdot 3 Nb_2O_5 \cdot 50.5 SiO_2$ (type II glass, synthesis

under an argon atmosphere), their electronic conductivity is four orders of magnitude higher than those of their ionic components. To ensure a reversible contact with the glass membrane, a chemical coating of silver or copper is deposited on the inner surface of the glass electrode in contact with the metal wire.

These glass electrodes can be simply prepared with a glassblower torch. Their chemical inertness and sufficient exchange currents cause them to behave like noble metal electrodes in reversible redox systems such as $Fe^{3+,2+}$, $Fe[CN]_6^{4+,3+}$, quinone/hydroquinone, etc. In addition, they are insensitive to the gaseous components of redox systems such as $(1/2) Cl_2(g)/Cl^-$, $H^+/(1/2)H_2(g)$, or $O_2(g)/H_2O$. Not only are these electrodes well suited to measure redox potentials in various systems under aerobic conditions, but they can also be selected for systems where other electrodes commonly used for redox measurements faces difficulties. In the study of the system Ce^{4+}/Ce^{3+} (redox potential $E_H = 1.44$ V), the use of Pt electrodes, for instance, suffers from two side processes, namely, oxidation of the electrode material along with decomposition of cerium solutions on the Pt surface with evolution of oxygen from water, whereas a glass electrode is free of such limitations.

These glasses are actually semiconductors because their conductivity is electronic in nature. When used to prepare electrodes, they result in a special sensitivity to the level of the redox potential of the solution. By *selectivity* we mean here that the electrode can partially equilibrate with a system i regardless of the presence of a competing system j [13]. The effect is due to special features of the energy distribution among the charge carriers in the surface layers such that n -type semiconductors are selective to redox systems with a low E_H , e.g. -0.38 V for the Eu^{3+}/Eu^{2+} system, whereas p -type semiconductors are selective to high E_H systems, e.g. 1.44 V for the Ce^{4+}/Ce^{3+} system. In both cases the E_H values are outside the thermodynamic stability limits of water [14]. Glass electrodes are thus valuable for these applications because they are indifferent in a wide range of redox potentials and pH solutions, thanks to their high chemical stability, as illustrated by kinetic parameter study of the reaction $Ti^{3+} + O_2$ (for the system Ti^{4+}/Ti^{3+} , $E_H = -0.11$ V) in the presence of molecular oxygen in the solution [15].

3 Glass Structure as Viewed by the Glass Electrode

3.1 The Electrode Method

From the middle of the 1950s, the Nikolskii–Schultz School carried out systematic research on electrode properties of glasses of $M_2O-R_xO_y-SiO_2$ systems [16], where

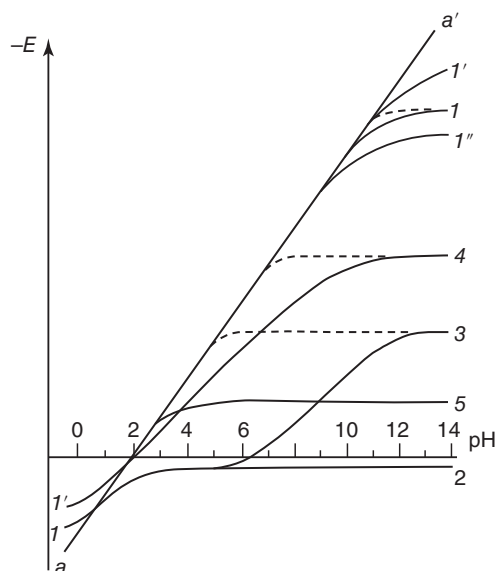


Figure 3 Structural role of elements as determined from electrode properties of alkali silicate glasses. Solid lines: experimental E -pH curves; dashed lines: calculated values with Nikolskii's Eq. (9). Glasses: M_2O - SiO_2 . M_2O is the first modifier, SiO_2 is the first network former (1); M_2O - R_xO_y - SiO_2 . R_xO_y role: 1', 1'' is the second modifier; 2, 3, 5 are the second network formers; and 4 is the intermediary. The straight line aa' is the hypothetical H^+ function $c_{M^+}^{sol} = \text{const}$.

$M = Na$ or Li was the initial network modifier, Si the initial network former, and R any other element incorporated. The electrode method to study glass structure is based on the fact that, when part of SiO_2 is replaced by R_xO_y , differences in the pH response (E -pH curves) with respect to that of a binary M_2O - SiO_2 glass depend on whether the element R is another network former or another network modifier or is playing an intermediate role.

Ions in glass mutually polarize each other. Here binary alkali silicate glasses M_2O - SiO_2 (15–33 mol % M_2O ; $M = Li, Na$) will be used as references for subsequent comparison. One can consider that their electrode potential is determined only by H^+ ions up to pH 8–10, whereas M^+ metal ions begin to influence the potential at higher pH values (Figure 3, curve 1). The reason is that a binary glass has weak acidic ionogenic groups $[SiO_{3/2}]OH$. The bond strength of hydrogen in these groups is mainly covalent and very strong.

3.2 Effect of a Second Network Modifier

If a network modifier is added as a third oxide R_xO_y to the glass, the ion R^{z+} placed in the environment of an $[SiO_{3/2}]OM$ group polarizes the $O-M$ ($O-H$) bond. This effect is either weaker or stronger than that of the initial M^+

cation. The former case for instance applies to Cs , Ca , or Ba : the $O-H$ bond then becomes stronger, and the linear H^+ response of the glass electrode extends into the higher pH region (Figure 3, curve 1'). For Mg or Be , the opposite holds true: the $O-H$ bond weakens, and the H^+ response linear region narrows down (Figure 3, curve 1''). These phenomena are named the *electrode effect of the second modifier* [16].

3.3 Effect of a Second Network Former

Addition of network-forming ions R^{z+} has dramatic effects as their incorporations into the silicate network induce changes in the coordination number k or in the interatomic distances $R-O$ inherent to the R_xO_y oxide. These cations R^{z+} have so strong polarizing effects that they form their own element silicate ionogenic groups $[SiO_{4/2}] - [RO_{k/2}]^{(k-z)-} (k-z) M^+$ (for simplicity, reference to $[SiO_{4/2}]$ in such groups will be omitted hereinafter). This case is in particular that of Al , B , Ga , and Fe ($z = 3$, $k = 4$) (Figure 3, curves 2 and 3), Sn and Zr ($z = 4$, $k = 6$) (Figure 3, curve 5).

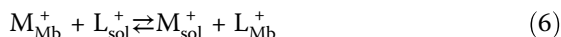
The subsequent exchange of M^+ for H^+ or $M^{+'}$ from the solution results in the formation of the $[RO_{k/2}]^{(k-z)-} (k-z) H^+$ (or $M^{+'}$) groups, which are strongly acidic in H^+ form. The $O-H$ and $O-M'$ bonds in these groups do not differ significantly either in their character (they are mostly ionic) or in their energy. This feature results in an early disruption of the H^+ response (at $pH = 1-3$). If a fairly small quantity (1–4 mol %) of the network-forming oxide R_xO_y is added, then the appearance of $[RO_{k/2}]^{(k-z)-} (k-z) H^+$ groups manifests itself as a "step" in the E -pH curve at pH values from 1–3 to 5–6, followed by a decrease of E caused by the predominance of silicate groups (Figure 3, curve 3). This response is akin to the titration curve of a mixture of strong and weak acids. At higher concentrations of the network formers, the glass electrode responds to pH changes only in the region of the strong acidic solutions, and it shows response to the M^+ ion at pH higher than 3 or 4. In Figure 3 this behavior corresponds to the horizontal parts of curves 2 and 5 at $c_{M^+}^{sol} = \text{const}$. Introduction of oxides of Y , La , and Ti and of some rare earth elements into the glass composition eliminates the acid error and gradually reduces limits of H^+ response. This is the *intermediator effect* (Figure 3, curve 4).

In such studies of E -pH curves for M_2O - R_xO_y - SiO_2 glasses, it was thus possible to determine successfully the structural role of the network-modifying, intermediary, and network-forming ions for about 30 different elements of the periodic system [16]. This method was thus applied to elucidate the structural role of a variety of oxides much earlier than made with direct, structure-sensitive methods (Section II).

4 Theories of the Glass Electrode

4.1 Nikolskii's Thermodynamic Ion-Exchange Theory

Experimental data accumulated in the 1920s gave a sound basis to the first theory of glass electrodes. As formulated in 1937 by Nikolskii [17], the idea that the primary phenomenon at work in both glass electrodes and other ion-selective electrodes is ion exchange has gained general recognition. The ion-exchange equilibrium



is thus established between the glass membrane and the solution, so L^+ cations (H^+) also appear in the membrane. Identical cations also exchange between the membrane and solution



in reactions that are faster than ion exchange. The potential-determining equilibrium will be thus the reactions $H_{Mb}^+ \rightleftharpoons H_{sol}^+$ (7) and (8) in the regions of H^+ and M^+ response, respectively.

It is within the framework of this thermodynamic ion-exchange theory that Nikolskii derived the following equation for the glass electrode potential:

$$E = E^0 + 2.3 \frac{RT}{F} \log (a_{H^+} + K_{H^+,M^+}^{exch} a_{M^+}), \quad (9)$$

where E is the emf of a galvanic cell (2), the parameters E^0 , R , T , F are as defined in Eq. (3), and a_{H^+} and a_{M^+} are the ion activities in the solution.

The exchange constant then is

$$K_{H^+,M^+}^{exch} = \frac{a_{H^+}^{sol} a_{Na^+}^{Mb}}{a_{Na^+}^{sol} a_{H^+}^{Mb}} = \exp \frac{(\mu_{H^+}^{0,Mb} - \mu_{Na^+}^{0,Mb}) - (\mu_{H^+}^{0,sol} - \mu_{Na^+}^{0,sol})}{RT}, \quad (10)$$

where the difference between the standard chemical potentials of the ions in the glass membrane and in the solution $\mu_{i^+}^{0,Mb}$, $\mu_{i^+}^{0,sol}$ reflects the bond-strength differences in these phases.

This constant characterizes the sorption selectivity of the ions by the membrane from the solution as well as the position of the transition region [17]. It is the "influence factor" of the M^+ ion on the H^+ response of the glass electrode that has actually different meanings in different theories.

4.2 Evolution of the Theory

An equation such as (9) cannot describe the whole experimental E -pH curves, in particular, the extended transition from one response to another as well as the stepwise

pH response. These limitations stimulated further development of the theory through the rejection of two important assumptions made by Nikolskii to derive Eq. (9). The first was the unity activity coefficients of both H^+ and M^+ ions in glass, which meant that the activity coefficients γ_i 's were assumed independent of the degree of substitution of one kind of ion by another. The second was the assumption that the sum of the ions concentration in glass (or in the membrane) is constant:

$$c_{H^+}^{Mb} + c_{M^+}^{Mb} = c_R^{Mb} = c^0,$$

where c_R^{Mb} is the concentration of the fixed anionic sites in the membrane.

Two approaches may be distinguished in the subsequent evolution of the theory. On the one hand, the assumption made by G. Eisenman et al. [18, 19] about the nonideality of a glass membrane, i.e. $a_{i,Mb} = c_{i,Mb}^n$, where the parameter n relates the activity of the ion to its concentration, allowed a smooth transition from H^+ to M^+ response to be described successfully.

With another approach, the same result was obtained by Nikolskii et al. [16] on the basis of the concept of various ionogenic groups in glass and their dissociation constants. Moreover, this theory successfully explained the stepwise pH response illustrated by curve 3 in Figure 3.

The concept of the potential of a glass electrode as a phase boundary potential was replaced by the idea of a membrane potential, i.e. a potential drop accounting for those occurring at phase boundaries as well as for diffusion potentials in surface layers on both sides of the glass membrane. Equilibrium at the boundary, which determines the phase boundary potential, then specifies the boundary conditions for the diffusion potential [20]. Experimental evidence for these two phase boundaries has come from studies of the glass electrode potential dynamics and the actual composition of surface layers of some alkali aluminosilicate glasses after the transfer of the glass electrode from HNO_3 or MNO_3 solutions into an $AgNO_3$ solution, and vice versa [21].

4.3 Nikolskii-Eisenman Equation

In many respects the electrode properties of glasses such as the extension and slope of the electrode response or its selectivity depend on the mobilities of ions and on the mechanism of their transport in glass. The Nikolskii-Eisenman equation [16, 19] describes the glass electrode potential as a membrane one:

$$E = E^0 + 2.3 \frac{RT}{F} \log \left[a_{L^+}^{1/n} + \frac{\bar{u}_{M^+}}{\bar{u}_{L^+}} (K_{L,M}^{exch} a_{M^+})^{1/n} \right]^n. \quad (11)$$

Unlike Eq. (9), this expression takes into consideration the nonideality of the glass membrane (through the factor

n), and it also includes the ratio of the ions mobilities in the membrane changing the significance of the “influence factor.” In Eq. (11), E, E^0, R, T, F, a_{L^+} , and a_{M^+} are defined as above, whereas $\bar{u}_{M^+}, \bar{u}_{L^+}$ are the ion mobilities at the glass surface layers, their ratio being assumed to be constant.

The product $(\bar{u}_{M^+} / \bar{u}_{L^+})^n K^{\text{exch}}$ determined from potentiometric measurements is named the potentiometric selectivity coefficient $K_{L/M}^{\text{pot}}$ (or $K_{L/M}^{\text{sel}}$), whereas $K_{L/M}^{\text{pot}}$ and n are empirical parameters, which are characteristic for a particular glass for any given pair of cations. If L^+ designates H^+ , then $n > 1$ and Eq. (11) may be fit to experimental curve. If L^+ is Na^+ and M^+ is K^+ , then as a rule $n = 1$. This equation describes well the glass electrode behavior in the regions of pure H^+ (at $a_{H^+} \gg K_{H/M}^{\text{pot}} a_{M^+}$) or pure M^+ responses (at $a_{H^+} \ll K_{H/M}^{\text{pot}} a_{M^+}$). It also describes well a smooth transition from H^+ to M^+ responses, hence challenging Nikolskii's equation in [17], which did not consider a factor n and predicted a sharp transition from one response to another.

4.4 Processes in the Surface Layers of Glass and the Glass Electrode Potential

A deeper insight into the operation of the glass electrode was achieved through observations of the concentration profiles of ions in glass layers that were altered by interaction with the solution (Figure 4). Along with studies of chemical and electrochemical processes at the glass–solution boundary, these observations have led to

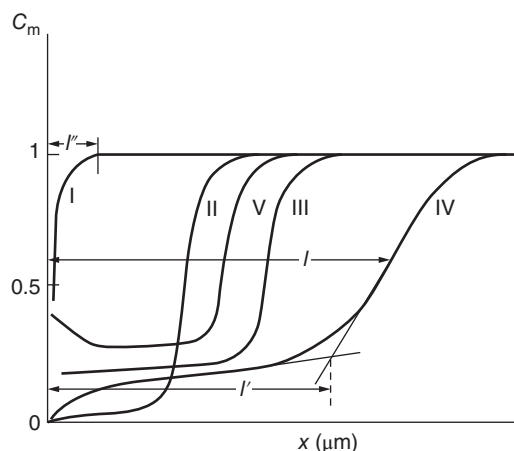
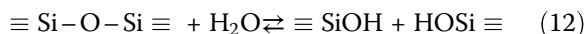


Figure 4 Typical profiles of ion concentrations in the surface layers of glass. I: Steep gradient of Me^+ characteristic of durable lithium silicate glasses, reflecting a “simple” ion interdiffusion. II, III, IV, and V: S-shaped profiles characteristic of sodium silicate and aluminum sodium silicate glasses, indicating ion interdiffusion accompanied by other processes such as dissolution of the glass network or its hydrolysis. The thicknesses of the surface layers involved can be defined as l, l', l'' .

a better understanding of the dynamics of the glass electrode potential and other properties of the glass surface. It has in particular been established that hydrolysis/condensation reactions of the form



and processes such as microphase separation accompany the interdiffusion process in the surface layers that cause their structural transformations and changes in site numbers R^- , so the glass electrode potential changes with time. For this reason, Doremus [22] proposed an equation for the potential of glass membranes consisting of two parts differing in their composition and/or in structure and, accordingly, by their values $\bar{u}_{M^+}, \bar{u}_{L^+}$ and $K_{L/M}^{\text{exch}}$, i.e. $K_{L/M}^{\text{pot}}$. Changes within the interfacial boundary region may cause E change to with t . A multilayer model of an inhomogeneous altered surface layer with m ($1 \dots k \dots m$) sublayers has been proposed [21] to account for this dependence. Experiments have indeed shown that the dynamics of glass electrode potential correlates with the temporal changes in the ionic composition of the glass surface layers.

4.5 Nernst–Planck–Poisson Model

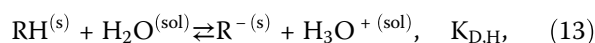
Another modern potentiometric model [23] regarded as promising uses the Nernst–Planck–Poisson (NPP) system of equations to simulate the nonequilibrium response. Unlike in the phase boundary model, electroneutrality and steady-state/equilibrium assumptions are abandoned so that the space and time domains are accessed. The NPP model describes a system consisting of m layers (phases) within which the concentration changes of r components – ions or uncharged chemical species (as it is done in multilevel model) – and a change of the electrical field in space and time take place. The NP equation describes the transport of ions by diffusion and migration, whereas the P equation governs the electrical interaction of the species. The model predicts well an ion-sensor response and also the selectivity and the variability of the lower detection limit over time.

4.6 Baucke's Dissociation Mechanism

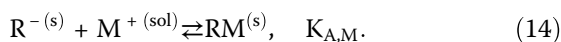
Using high-resolution techniques of ion bombardment for spectrochemical analysis (IBSCA) and nuclear reaction analysis (NRA) to study glass surfaces, Baucke [24] gave a most detailed description of the surface layers for lithium silicate glass. He described the state at the glass–solution interface as a dynamic equilibrium both in terms of thermodynamics and electrochemical kinetics. He pointed out that the electrochemical mechanism of the glass electrode potential formation is a consequence

of a process termed *charge division* at the boundary (the dissociation mechanism).

Uncharged surface groups RH and RM are formed because of glass interaction with the solution. Their dissociation results in the appearance on the glass surface of a minute concentration of negatively charged groups R^- , e.g. SiO^- or $SiOAl^-$, depending on the compositions of the glass and of the solution (and in particular of its ion concentrations). These anionic groups provide a density of negative charges on the surface and, therefore, give rise to a negative potential of the glass membrane with respect to that of the solution. Both the concentration of the charged groups and the glass electrode potential are functions of the solution composition $E = f(\text{pH}, \text{pM})$. The reactions of dissociation (and association) of the glass surface groups are in cumulative equilibrium:



and



From the respective equilibrium constants of these reactions, $K_{D,H}$ and $K_{A,M}$, Baucke defined a “selectivity product,” namely, $(K_{D,H} \bullet K_{A,M})$. This product plays a role similar to that of K^{exch} in Nikolskii’s Eq. (9), i.e. it determines whether or not a glass electrode exhibits a pH or pM response and it characterizes the position of the transition region. According to Ref. [24] this “selectivity product” is constant and its magnitude is equal to 10^{-12} .

A thermodynamic treatment of the acid dissociation equilibrium, Eq. (13), yields the equation

$$E = E_H^0 + \frac{RT}{F} \ln \frac{a_{R^{-(s)}}^{(s)} a_{H_3O^+}^{(s)}}{a_{RH}^{(s)} a_{H_2O}^{(s)}} = E_H^0 + 2.3 \frac{RT}{F} \log \frac{a_{R^{-(s)}}^{(s)}}{a_{RH}^{(s)} a_{H_2O}^{(s)}} - \text{pH}, \quad (15)$$

which thus describes the linear pH dependence of the glass membrane potential as it is usually known. This equation also indicates that the potential of the glass is determined by the minute concentration of the dissociated groups, R^- , which are bound to the glass surface and are thus in contact with the solution. Among the significant features of this approach is the theoretical proof of the fact that the experimental slopes of the E –pH (pM) curves are slightly lower than “ideal” ones (namely, 59.16 mV/pH at 25 °C) by lying in the range 58–59.1. This difference exists because the change in the activity of ions H^+ and M^+ is connected with the activity change in the other members of the equilibrium.

5 Perspectives

Elaboration of new glass compositions along with progress in electronics and instrument manufacturing has produced glass electrodes with more robust membranes that could be operated outside the laboratory in a such different contexts as chemical industry, environmental and pollution control, medicine, oceanography, biology, or life sciences. Hence, only temperature probably is a fundamental parameter now measured more frequently than pH! Development of new special glasses for electrodes with a reversible solid contact will expand further applications in wider temperature ranges with the same excellent reproducibility.

The stability of these glass electrodes at high temperature makes it possible to sterilize them with steam under pressure (150 °C) and, therefore, to apply them in biotechnical pH monitoring. They will, for instance, be commonly used all over the world to monitor pH and pM for evaluation of the health level in animals and humans (for example, in their aggressive intestinal tract). Thanks to their insensitivity to gaseous components, redox glass electrode will in addition be utilized for measuring redox potentials in microbiological systems under aerobic conditions where interferences with the system O_2/H_2O will be avoided. Likewise, these electrodes will be fit for measuring pH in Antarctic waters below 0 °C as well as up to 3000 atm in deep ocean depths down to the Marianas Trench (11 km)!

Baucke studies have actually represented a significant advance in understanding the operational mechanism of glass electrode. From a theoretical standpoint, however, the current framework does not account yet consistently for the dependence of the glass electrode properties on the composition and structure of the glass (especially those properties governed by the ionic mobility), for the extended interval of glass electrode potential in the transition region, or for the dynamics of the potential at transition from one response of glass electrode to another. One can thus surmise that a unified theory of the glass electrode will be created on the basis of Nikolskii–Eisenman theory, Baucke’s approach, and multilayer and Nernst–Planck–Poisson models.

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5.9

Electrochemistry of Oxide Melts

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1 Introduction

Synthetic as well as natural glasses generally contain more or less high fractions of *polyvalent* elements, which may thus occur in at least two different oxidation states even if only under extremely oxidizing or reducing conditions. In industry, these elements are either impurities in the raw materials or added on purpose to the glass batch, for example, as fining or coloring agents (Chapter 1.2). The main physical property of a glass influenced by the redox state is the color, i.e. the transmissivity of light in certain wavelength ranges. To a high extent, this feature determines product quality and may in particular reflect the temperature distribution within the melting tank. Other important properties of glasses that depend upon polyvalent elements are fluorescence and solarization.

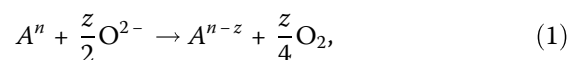
Whether for fundamental or industrial reasons, polyvalent elements and their redox properties must be accurately characterized. If electrochemical methods are particularly valuable in these respects, it is because they are well suited for determining not only the thermodynamics of redox equilibria but also the diffusion coefficients of redox couples or the concentrations of polyvalent species even in glasses contained in melting tanks. A significant advantage of these methods is that they are in principle much faster than those involving redox equilibration experiments. As originally developed to study aqueous or organic solutions, electrochemical methods require good ionic conductors, that is, melts containing alkali oxides at concentrations higher than 10 mol % whose conductivity thus is purely cationic ([1], Chapter 4.2).

To review these methods in this chapter, it will be useful to summarize first the basics of redox thermodynamics, referring the reader to Chapter 5.6 for a more complete account. After a brief summary of experimental methods, the thermodynamic determination of redox standard potentials and equilibrium constants will be described. Diffusion coefficients will then be dealt with, followed by voltammetric chemical analyses. Finally, the principle of impedance spectroscopy will be discussed.

Because ionic conductivity strongly depends on temperature, the temperature range for which a specific method can be applied is restricted. As a general rule, the larger the ionic conductivity, the smaller the minimum temperature at which a certain electrochemical method can be applied. An upper limit for an electrochemical measurement is only imposed by the chemical and mechanical stability of the used materials. Since electrodes are generally made out of platinum, the upper limit should be about 1650 °C. The minimum possible temperature also depends on the method used. For example, simple potentiometric experiments, such as oxygen activity measurements, are possible at lower temperatures than voltammetric measurements where current voltage curves are recorded.

2 Thermodynamics of Redox Equilibria

At high temperatures, polyvalent elements in reduced and oxidized forms build equilibria with the oxygen physically dissolved in the melt (O^{2-}):



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where n is the number of transferred electrons and A^n and A^{n-z} are the redox species in its oxidized and reduced state, respectively. The constant of this equilibrium depends on both temperature and melt composition:

$$K(T) = \frac{a_{A^{n-z}} \cdot a_{O_2}^{z/4}}{a_{A^n} \cdot a_{O_2}^{z/2}}, \quad (2)$$

where a_i is the activity of species i . Except for silver in certain systems (see Section 5), the equilibrium described by Eq. (1) shifts to the right with increasing temperature. In other words, the reduced state is favored with increasing temperature since production of gaseous oxygen causes the large entropy increase associated with the stable high-temperature state by Le Chatelier's moderation principle.

Because the O^{2-} species do not occur in noticeable quantities in most glass compositions, and its activity is in addition unknown, it is more suitable to describe the redox equilibrium by another equilibrium constant $K'(T)$ defined as

$$K'(T) = K(T) \cdot a_{O_2}^{z/2} = \frac{a_{A^{n-z}} \cdot a_{O_2}^{z/4}}{a_{A^n}}, \quad (3)$$

which also depends upon melt composition.

In most glass melts, the concentration of physically dissolved oxygen is much smaller than those of polyvalent ions, so the equilibrium described by Eq. (1) does not shift noticeably upon quenching if no other redox pair is present in the melt [2]. This is the reason why one can determine redox equilibrium constants by equilibrating a melt with an atmosphere of known oxygen partial pressure, quenching the sample and analyzing the A^n/A^{n-z} ratio by appropriate physical or chemical means. But this procedure is time consuming because the needed diffusion of oxygen into or out of the sample tends to be slow under conditions where speeding up of the equilibration process by convection is not possible because of a high melt viscosity. Although the quantity of melt equilibrated with the atmosphere in these experiments is usually as small as a few grams, one should always ensure that equilibrium with the atmosphere is actually reached. An alternative procedure is to measure the oxygen activity of the melt with a ZrO_2 -based sensor. In the literature, numerous studies on redox equilibria relying on such equilibration methods have been reported (e.g. [3]).

In the last two decades, however, redox equilibria have frequently been studied electrochemically [4, 5]. Although the most common method is square-wave voltammetry, impedance spectroscopy is also used. To perform these measurements, electrodes are inserted into the melt, and measurements are directly carried out, typically in the 1000–1600 °C range. In addition to the

redox equilibrium data, diffusion coefficients are also derived from the recorded voltammograms.

According to Eq. (1), the ratio A^n/A^{n-z} depends on the gas atmosphere, temperature, and, furthermore, melt composition. From the equilibrium constant $K'(T)$, the standard Gibbs free energy, $\Delta G^\circ(T)$, can be obtained. If its temperature dependence is also determined, then the standard enthalpy, ΔH° , and entropy, ΔS° , can also be derived from

$$\Delta G^\circ(T) = \Delta H^\circ - T\Delta S^\circ = -RT \ln K'(T), \quad (4)$$

where R is the gas constant. In addition, the standard potential E_0 of the redox pair and its temperature dependence can be determined because it is related to the standard Gibbs free energy, $\Delta G^\circ(T)$, by

$$\Delta G^\circ(T) = -nFE_0(T), \quad (5)$$

where F is Faraday constant and n is the number of transferred electrons.

Empirically, available experimental data have been used to account for the dependence of redox equilibria on melt composition in terms of formulae that account for the contribution of each component by an incremental system, generally with the assumption of a linear effect for each of them. Actually, however, this approach is highly questionable at least for elements such as alumina or boron whose oxygen coordination numbers and structural role vary with the overall glass composition (Chapters 2.4, 7.6) as also mentioned below.

3 Experimental Aspects

In usual laboratory electrochemical measurements, from 50 to 250 g of glass is melted between 1000 and 1600 °C, depending on composition, in a platinum crucible in a high-temperature furnace (for instance, with $MoSi_2$ heating elements). The highest signal-to-noise ratios are obtained if the power supply of the furnace delivers a d. c. voltage. For oxygen activity measurements, the potential between a zirconia probe and a platinum electrode may, for instance, be measured (Figure 1). Whereas the zirconia electrode must be as large as possible, the wire forming the three-phase boundary melt/Pt/air must be as thin as possible to minimize oxygen transport.

If air is used as a reference gas, the oxygen activity, a_{O_2} , of the melt can be calculated with

$$E = (RT/4F) \ln (a_{O_2}/0.21 \text{ bar}). \quad (6)$$

It follows that measurements of a_{O_2} at varied temperatures also enable ΔH° to be calculated.

For voltammetric measurements (Figure 2), three electrodes are inserted into the melt from the top: a platinum

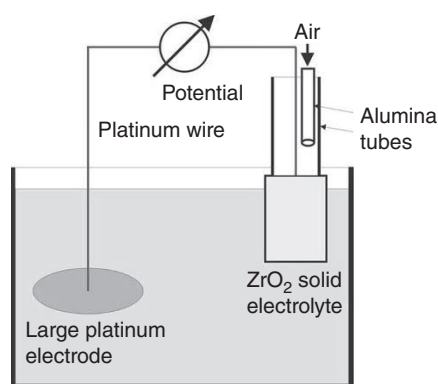


Figure 1 Experimental set up for measurements of oxygen activities in a glass melt.

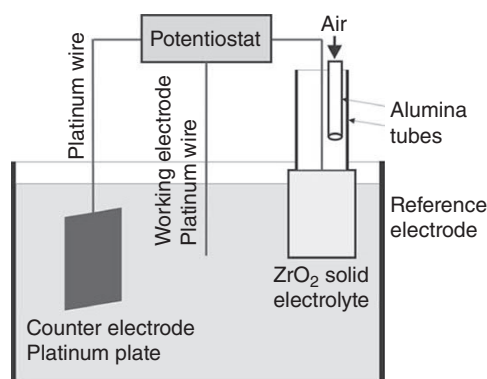


Figure 2 Experimental set up for voltammetric measurements in glass melts.

wire (1 mm in diameter) as the working electrode, a platinum plate as a counter electrode (size: 2 cm²), and a ZrO₂-based reference electrode flushed with air. These three electrodes are connected to a potentiostat, which is the main part of the electronic equipment because it ensures that the potential between the working and reference electrodes is always equal to the required value. The potentiostat is further connected to a computer, which also controls the desired time dependence of the potential and records the current. The fundamentals of this method are well documented in literature (e.g. [6]).

In square-wave voltammetry, the most frequently used technique, the potential–time dependence is a staircase ramp upon which a rectangular wave ($\tau = 10\text{--}400$ ms, potential amplitude $\Delta E = 100$ mV) is superimposed. One measures the current after each half-wave and then calculates the difference between two consecutive values to derive the standard potential of the redox pair considered. In simple cases, this potential is given by the maximum observed in the current–potential curve (Figure 3). The situation is more complicated if two redox pairs are

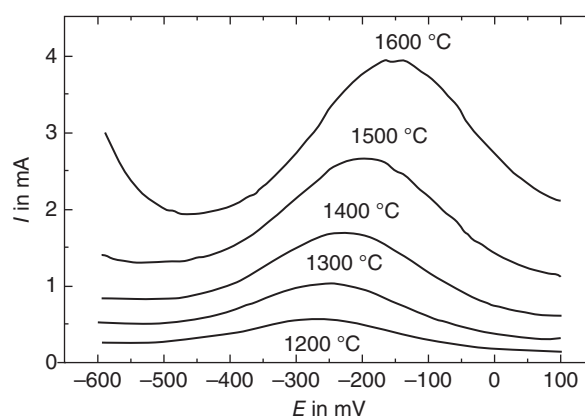


Figure 3 Effects of temperature on peak potentials in voltammograms recorded for a 10 Na₂O·10 MgO·10 Al₂O₃·70 SiO₂ (wt %) melt doped with 0.25 mol % Fe₂O₃ [7].

present with overlapping current–potential curves or in any other nonideal case, for instance, if adsorption at the electrode takes place [8]. As described in detail in the literature [9], it is best to deconvolute the curve in terms of experimentally recorded matrix currents and theoretically calculated current–potential curves [6] of the particular electron transfers. Equilibration with the surrounding atmosphere is in fact not necessary because the working electrode has a starting potential – usually 0 mV vs. the zirconia-air electrode – which yields the same redox ratios as achieved upon equilibration with air.

From the peak current densities, i_p , diffusion coefficients can in addition be obtained with

$$i_p = \text{const} \cdot D^{1/2} \cdot C_o \cdot \Delta E \cdot \tau^{-1/2}, \quad (7)$$

where C_o is the total concentration of the polyvalent ion, D is the mean diffusion coefficient of its oxidized and reduced species, ΔE is the pulse potential, τ is the step time of the square wave, and const is equal to $0.31 \cdot \pi^{-1/2} \cdot F^2 \cdot n^2 / (RT)$.

In summary, a simple potential measurement enables first the oxygen activity of the melt to be determined and then the redox ratio to be calculated if the thermodynamics of the redox pair considered is known.

4 Standard Potentials and Equilibrium Constants

To verify the validity of the determined dependence of a redox ratio on oxygen activity, one dopes the melt investigated with the polyvalent element of interest and equilibrates it under different oxygen fugacities at the same temperatures. The redox ratios are then determined independently, for instance, by spectroscopic methods. In a

plot of $\log ([A^{n'}/[A^{n+z}]]$ against $\log (a_{O_2})$, a_{O_2} = oxygen activity, the results define a straight line with an $n/4$ slope. As a matter of fact, all redox pairs studied in this way conform to Eq. (1), so this relationship is experimentally well proved [5].

As a first example, the square-wave voltammograms recorded at different temperatures from a potential of 0 mV for an iron-doped (Na,Mg) aluminosilicate are shown in Figure 3. All curves display a distinct maximum caused by the reduction of Fe^{3+} to Fe^{2+} :



With decreasing temperatures, the peak potential becomes increasingly negative, varying from about -145 mV at 1600°C to -225 mV at 1200°C , thus indicating a shift of the iron redox equilibrium toward the oxidized Fe^{3+} state. In parallel, the strong decrease observed for the peak currents is caused by decreasing diffusion coefficients. As for the final increases of the current at potentials more negative than -500 or -600 mV (depending on temperature), they are due to partial decomposition of the melt into platinum silicide.

More comprehensive results illustrate the effects of changes of either composition or temperature on iron redox equilibrium. The effects on potentials of the substitution of MgO for SiO_2 at 1600°C (Figure 4) [7] are in fact similar to those of decreasing temperatures (Figure 3): increasing MgO concentrations yield more negative potentials through shifts toward the Fe^{3+} state, whereas diffusion coefficients increase notably. This similarity is borne out by comparisons made between the effects of temperature and MgO concentrations on peak potentials whose variations are approximately linear in both cases (Figure 5). The effect of glass composition on the peak potentials also enables conclusions to be derived on the melt structure at the respective temperature, for example,

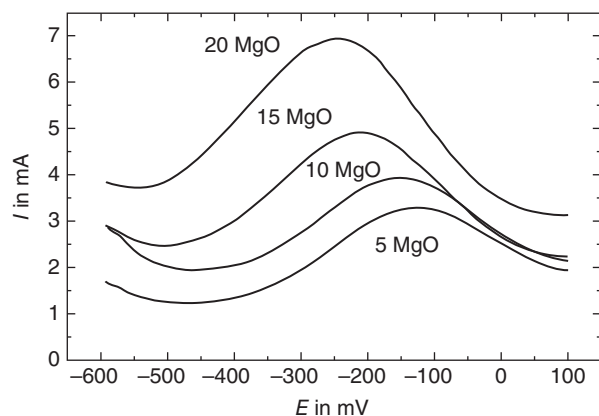


Figure 4 Effects of (MgO, SiO_2) substitution on peak potentials in voltammograms recorded at 1600°C for $10 Na_2O \cdot x MgO \cdot 10 Al_2O_3 \cdot (80 - x) SiO_2$ melts doped with 0.25 mol % Fe_2O_3 [7].

on the way in which an increasing Al_2O_3 concentration causes Al to be no longer solely incorporated in tetrahedral coordination.

Copper raises more difficulties than iron because the initial reduction of Cu^{2+} into Cu^+ is followed by reduction of Cu^+ into metallic Cu, which can alloy with the Pt electrode. Because the second of the two peaks of voltammograms (not shown) thus has to be discarded, only the peak potentials of the first reaction are displayed in Figure 6 [10] against temperature for Cu-doped sodium aluminosilicate melts with varying Al/(Al + Si) ratios. In these instances, the measurements become increasingly inaccurate above 1000°C because of signal superimposition with matrix currents at positive potentials caused by the decomposition of the glass matrix and the resulting formation of gaseous oxygen. At all temperatures, the peak potentials increase with increasing Al_2O_3

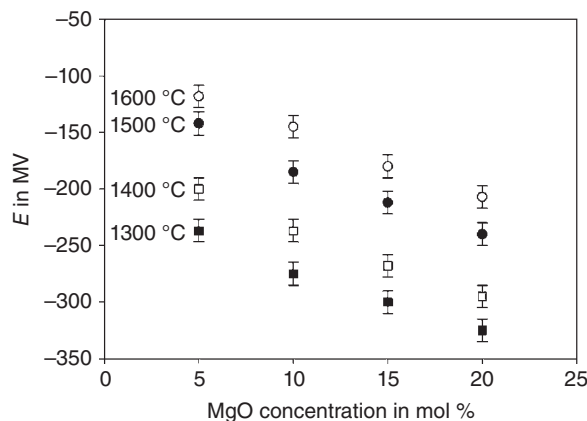


Figure 5 Voltammetric peak potentials as a function of the MgO concentration in glass melts with the basic compositions $10 Na_2O \cdot x MgO \cdot 10 Al_2O_3 \cdot (80 - x) SiO_2$ doped with 0.25 mol % Fe_2O_3 [7].

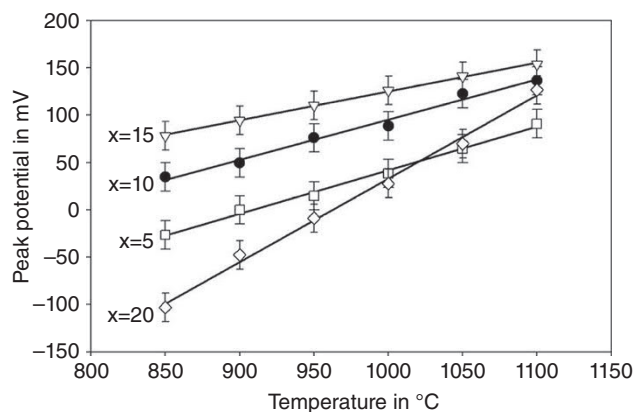


Figure 6 Voltammetric peak potentials of the Cu^+/Cu^{2+} peak as a function of the temperature in melts with the basic mol% compositions $26 Na_2O \cdot x Al_2O_3 \cdot (74 - x) SiO_2$ doped with 1 mol % CuO [10]. Solid lines: regression lines.

concentration from 5 to 15 mol % and then drop off so abruptly at higher contents that below 1000 °C the most negative peak potential is that of the sample with 20 mol % Al_2O_3 , because then Al_2O_3 is no longer incorporated solely in tetrahedral coordination. Within experimental errors, the potentials again depend linearly on temperature for all studied compositions. The slopes and intercepts of these lines thus directly yield the standard entropies, ΔS° , and enthalpies, ΔH° , of the redox reaction, whose highest absolute values are thus found for the 20 mol % Al_2O_3 sample.

Not surprisingly, a great many voltammetric measurements have been made on soda-lime-silica melts in view of their considerable industrial importance. A selection of data obtained for a variety of redox couples shows that, with the single exception of $\text{Ag}^\circ/\text{Ag}^+$, all peak potentials increase in absolute values with increasing temperatures with distinct but not so different slopes (Figure 7) [11]. As a result, the order of these redox couples remains basically the same at different temperatures. Of course, the values for a given redox couple reflect the particular manner in which both valences are incorporated in the melt structure. Hence, they depend on melt composition as already shown by Figures 4–6. For polyvalent elements

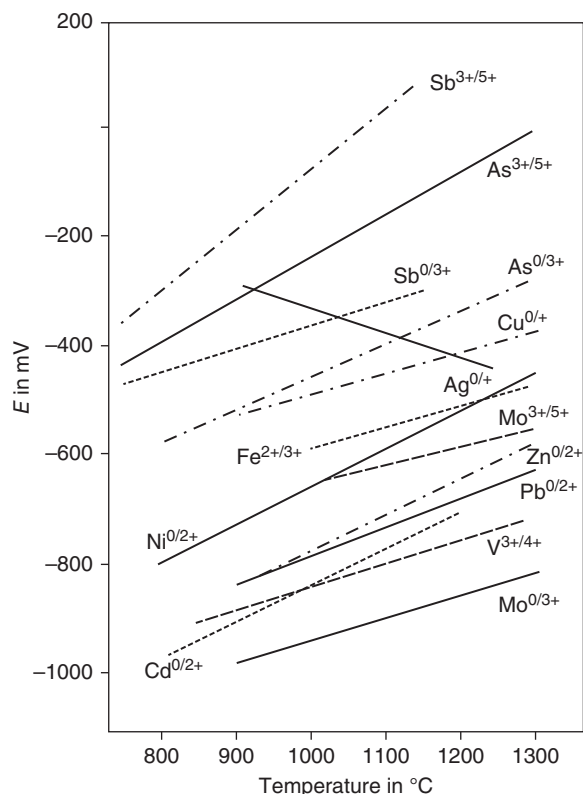


Figure 7 Effect of temperature on the electrochemical series for a glass with the composition 16 Na_2O ·10 CaO ·74 SiO_2 , doped with various types of polyvalent elements [11].

such as iron, tin, and copper, this effect has been studied in detail, so structural models for their incorporation have been proposed [1, 9]. From the broad variety of glass compositions investigated for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple, a model of prediction of the peak potential, for instance, has relied on sodium and aluminum speciation to yield

$$E_p(1300^\circ\text{C}) = a + b[\text{Na}_2\text{O}]_{\text{NBO}} + c[\text{Na}_2\text{O}]_{\text{Al}} + d[\text{MgO}] + e[\text{CaO}] + f[\text{Al}_2\text{O}_3]_t + g[\text{Al}_2\text{O}_3]_o + h[\text{SiO}_2], \quad (9)$$

where $[\text{Na}_2\text{O}]_{\text{NBO}}$ and $[\text{Na}_2\text{O}]_{\text{Al}}$ are the Na_2O concentrations of network-modifying and Al charge-compensating sodium, respectively, and $[\text{Al}_2\text{O}_3]_t$ and $[\text{Al}_2\text{O}_3]_o$ are the Al_2O_3 concentrations of tetrahedral and octahedral aluminum, respectively. The fit parameters are $a = 20$ mV and $b = 8.76$, $c = 3.42$, $d = 7.84$, $e = 11.19$, $f = 2.7$, $g = 7.34$, and $h = 2.72$ mV/mol % [1]. Other empirical formulae have been proposed in narrower composition ranges, from which the redox ratios can also be calculated from the glass composition and the oxygen activity. [7, 9]. The $\text{Ag}^\circ/\text{Ag}^+$ redox potential is a special case because it decreases with increasing temperature in Al-free melts (Figure 7), as already noted, and also below 1100 or 1200 °C in aluminosilicate melts before increasing “normally” at higher temperatures [12]. The Ag^+ ion can be a network-modifying or a charge-compensating cation for tetrahedral Al^{3+} , like alkali and alkaline earth cations with which it competes for bonding with either nonbridging or bridging oxygens. The complex voltammetric results thus point to complex structural interactions as function of both temperature and composition, which remain to be investigated specifically.

5 Diffusion Coefficients

In addition to peak potentials, square-wave voltammetric experiments have yielded a wealth of diffusivities for polyvalent elements. Some of them are represented in an Arrhenius plot for a standard soda-lime-silica glass in the rather wide 750–1300 °C range (Figure 8) [13]. As determined from fits made with Arrhenius equation to the experimental data, they range from 3×10^{-17} to 2×10^{-10} m^2/s :

$$D = D_o \cdot \exp(E_a/RT), \quad (10)$$

where E_a is the activation energy and D_o a pre-exponential factor.

At a temperature of 850 °C, the diffusion coefficients vary from 3×10^{-17} to 10^{-11} m^2/s , i.e. by more than six orders of magnitude. The largest are those of silver, known to be very mobile in a glass network, which, for example, makes this element highly suitable for ion

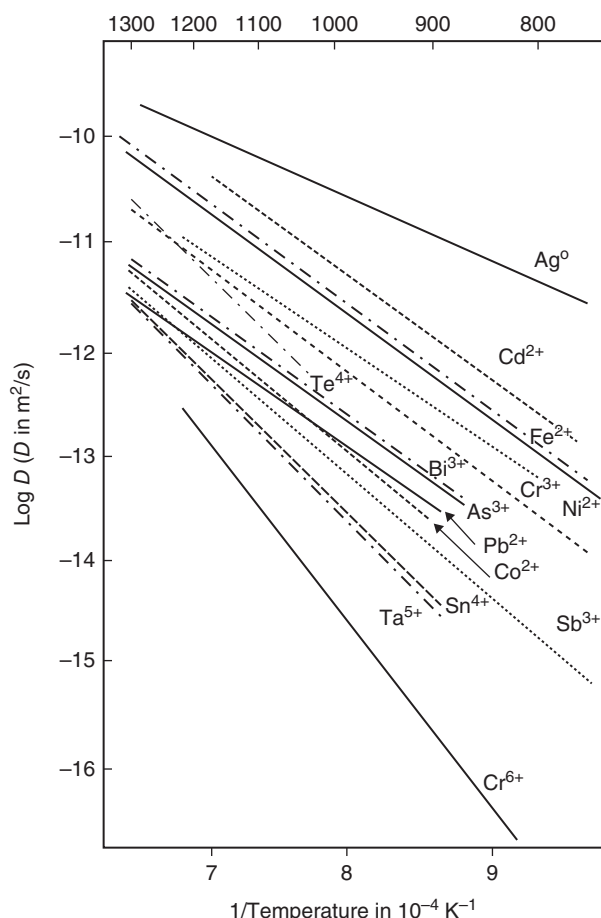


Figure 8 Arrhenius plot of the diffusion coefficients of various polyvalent elements determined in a glass with the basic composition 16 Na₂O·10 CaO·74 SiO₂ [13].

exchange. These diffusion coefficients are in the same order as those of other network modifiers such as alkalis.

The smallest values are those of Cr⁶⁺, which possesses a high charge and seems to be tightly bonded to the glass network. These diffusion coefficients are in the same range as those of silicon. The coefficients of ions with valences from 2 to 4 lie in between the values of Ag⁺ and Cr⁶⁺. As usual, diffusivities conform to a *compensation law* whereby the activation energies of faster diffusing species are lower and, conversely, those of slowly diffusing species are higher (Figure 8). But the large variations of the data plotted illustrate that Stokes–Einstein law is not generally valid because these diffusion coefficients should otherwise vary with the reciprocal of ionic radii, i.e. under no circumstances by more than one order of magnitude at the same temperature. Obviously, the way in which the respective redox species are incorporated in the melt structure plays an important part, and it is of course not simply determined by the ionic radius and the charge of the ion.

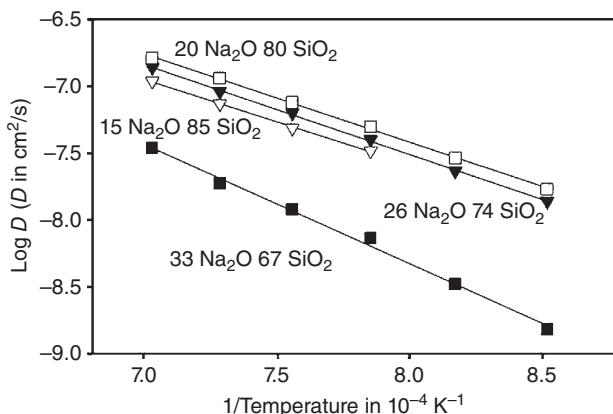


Figure 9 Arrhenius plot for the mean diffusion coefficients of Cu⁺/Cu²⁺ for different sodium silicate melts [14].

The strong effects of composition are illustrated by Arrhenius plots of the mean diffusion coefficients of Cu⁺/Cu²⁺ for different sodium silicate melts (Figure 9) [14]. In all cases, the temperature dependence is actually Arrhenian. Although similar values are found for Na₂O concentrations in the 15–26 mol % range, the diffusion coefficients are the smallest for the 15 mol % Na₂O melt, pass through a maximum at 20 mol % Na₂O, and then markedly decrease at higher contents. The surprising result is that copper diffusion coefficients are smaller than in the melt with the highest Na₂O concentration, i.e. with the lowest viscosity [14]. There are thus two competing regimes, namely, the first where Stokes–Einstein equation obtains and the second where copper becomes more strongly incorporated with increasing Na₂O concentration.

6 Voltammetric Sensors: Quantitative Determinations of Polyvalent Elements

Yet another application of voltammetry deals with the quantification of polyvalent elements, which can be performed directly, even in technical glass-melting furnaces where glasses such as green and amber are produced. These materials contain iron, chromium, and sulfur. Chromium occurs in three different valence states, namely, Cr²⁺, Cr³⁺, and Cr⁶⁺ and thus shows the two peaks of the redox pairs Cr^{2+/3+} and Cr^{3+/6+}. Altogether four voltammetric peaks are expected (two for chromium and one for both iron and sulfur) and are actually observed (Figure 10) [15]. The attributed peak potentials are known from laboratory studies of melts that contain only one of these polyvalent elements. If the attributions of peaks to the redox steps Cr^{6+/3+}, Cr^{2+/3+}, and Fe^{2+/3+} are clear, that of the sulfur peak is not. The shape of

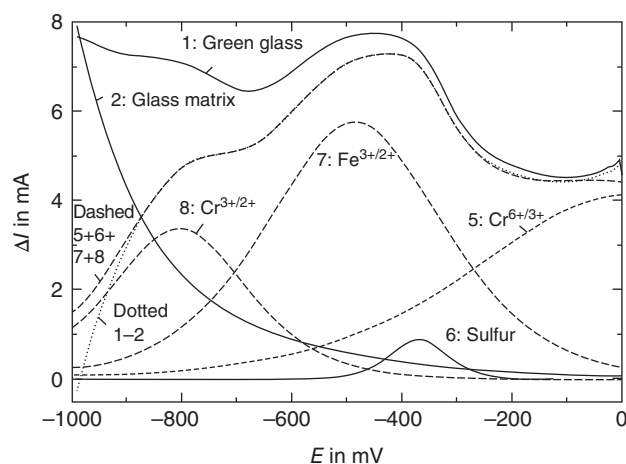


Figure 10 Voltammogram recorded for a green glass melt (curve 1) and a melt without any polyvalent element [15]. Difference curve (1-2) decomposed into contributions of $\text{Cr}^{6+/3+}$ (curve 5), sulfur (curve 6), $\text{Fe}^{3+/2+}$ (curve 7), and $\text{Cr}^{3+/2+}$ (curve 8). Curve 4, sum of the simulated curves 5-8.

the voltammogram is always the same, but the origin of the peak, i.e. the attributed redox pair, is not definitely known, possibly because electrode adsorption plays an important part.

But this limitation does not prevent sulfur from being quantitatively determined in the melt (Figure 10). First, a voltammogram is obtained for the melt under study and another for a melt with the same basic composition, but without any polyvalent elements. After subtracting the latter curve from the former, one decomposes with a least squares method the resulting difference into four bands whose peak potentials and full widths at half maximum yield the sought after contents of chromium, iron, and sulfur [15]. In the same base glass composition and at the same temperature, the peak potentials and half-widths do not depend on the respective concentrations.

7 Impedance Spectroscopy

The last technique to be presented is impedance spectroscopy, a fairly versatile tool to investigate glasses and melts. It is, for instance, extensively used in studies of corrosion processes (Chapter 5.10). Examples are corrosion of molybdenum electrodes in contact with glass melts or of ion conductive glass in contact with molten salts. Impedance spectroscopy is also commonly applied to investigate electrical relaxation phenomena, mostly at temperatures below the glass transition, and also phase separation when changes in ionic conductivity allow the temperatures of the transitions, or even their kinetics, to be determined.

By contrast, only a few studies have been performed with impedance spectroscopy on the thermodynamics and diffusion of polyvalent ions in glass melts (e.g. [16]). Here the same three-electrode equipment as used for voltammetric studies is suitable, and a large variety of methods is in principle possible. The method most frequently applied consists in superimposing on a given d.c. potential and a.c. potential with an amplitude of 5–50 mV and a frequency in the 10^{-2} – 10^6 s^{-1} range. Then one simply studies the effect of the d.c. potential by repeating the experiment at different values.

To obtain impedance spectra, the absolute value of the impedance and the phase angle or the real and the imaginary parts are measured and plotted for illustration. The next step involves setting up first a physical model of the processes at the working electrode and then an equivalent circuit composed of resistors, capacitors, and some other impedance elements. A suitable software is finally used to optimize the values of each impedance elements. If the simulated spectrum agrees with the measured values within the limits of the experimental error, the equivalent circuit is assumed to give an appropriate description of the electrode reactions.

Experiments done with three different d.c. potentials on a $16 \text{ Na}_2\text{O} \cdot 15 \text{ Al}_2\text{O}_3 \cdot 69 \text{ SiO}_2$ sample doped with 0.25 mol % Fe_2O_3 illustrate the procedure (Figures 11–13).

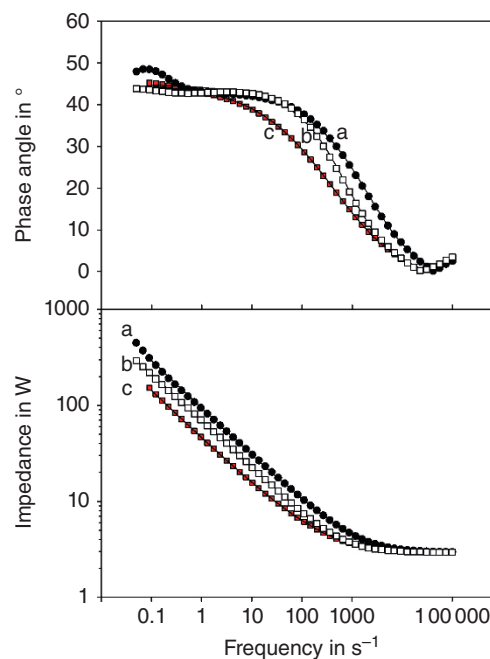


Figure 11 Impedance spectra in a melt with the basic composition $16 \text{ Na}_2\text{O} \cdot 15 \text{ Al}_2\text{O}_3 \cdot 69 \text{ SiO}_2$, doped with 0.5 mol % Fe_2O_3 recorded at 1500°C at different superimposed d.c. potentials of -400 mV (a), -150 mV (b), and 0 mV (c) [16]. Solid lines: simulated curves. Please note that the absolute values of impedance and phase angle are drawn.

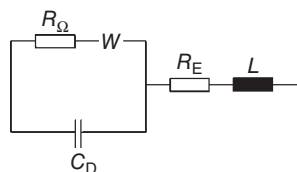


Figure 12 Equivalent circuit used to simulate the obtained impedance spectra [16]. L , inductivity; R_E , ohmic resistivity of the melt between the working and reference electrodes; R_Ω , resistivity due to the electron transfer reaction; C_D , double layer capacitance; and W , Warburg parameter.

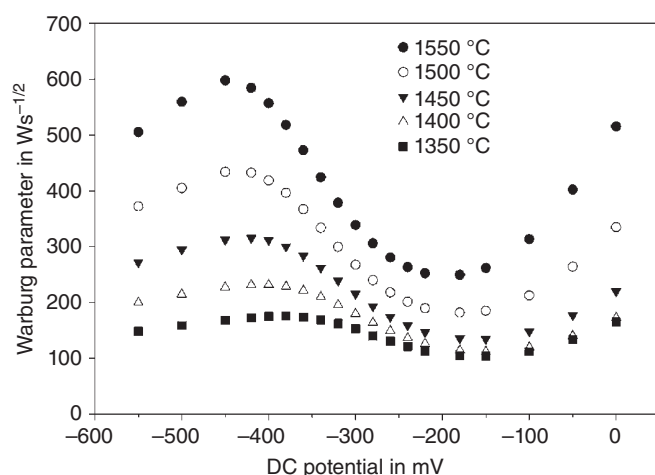


Figure 13 Dependence of the Warburg parameter on the superimposed d.c. potential at various temperatures for a $16\text{Na}_2\text{O} \cdot 15\text{Al}_2\text{O}_3 \cdot 69\text{SiO}_2$ base melt [16].

In spectra recorded at 1500°C in the 10^{-2} – 10^6 s^{-1} frequency range (Figure 11), the absolute value of the impedance is approximately constant and in addition does not depend on the d.c. potential at frequencies higher than $2 \times 10^3 \text{ s}^{-1}$. At lower frequencies, however, the differences become significant, the impedance increasing with the voltage applied. As for the phase angles, they are all negative up to a frequency of $2 \times 10^4 \text{ s}^{-1}$ above which they become positive (NB in Figure 11, the absolute values of impedance and phase angle are drawn). At the lowest frequency (0.1 s^{-1}), the absolute value of the phase angle is the largest and then decreases continuously until the minimum is reached. The curve obtained for -150 mV is clearly different from those recorded at the other potentials.

In a second step, the impedance spectra are simulated with an equivalent circuit (Figure 12), which is the simplest possible suitable to describe the electrochemical experiment. It is composed of the capacitance of an electrochemical double layer C_D , a resistor R_Ω (which is $>0 \Omega$ if the electrode reaction is kinetically hindered), a so-called Warburg impedance W (accounting for diffusion

processes), a resistor R_E (accounting for the limited ionic conductivity of the melt and increasing with decreasing electric conductivity), and an inductance L predominantly attributed to the wiring. For the melt compositions studied, the resistor R_Ω is negligibly small because the temperature is high enough that the electrode reaction is not kinetically hindered during the measurements.

That this equivalent circuit is appropriate is shown by the good agreement found between the simulated and experimental values (Figure 11). Interestingly, most elements of the equivalent circuit do not depend on the d. c. potential. Only the Warburg parameter W does so. It should possess a minimum at the standard potential of the electrode reaction, as borne out by the minima observed at five different temperatures between 1350 and 1550°C (Figure 13) where all points were extracted from individual simulations of the impedance spectra. Actually the Warburg parameter is the largest at 1550°C , where the diffusion coefficient of iron is highest, and decreases with decreasing temperatures. In all cases, a minimum is observed at potentials between -200 and -150 mV . The respective potential is identical with the respective standard potential.

8 Perspectives

Although the majority of electrochemical studies of glass melts have dealt with alkali or alkaline earth silicates and aluminosilicates, some have been carried out on phosphates or borosilicates. In the latter, voltammetric measurements are similar to those made on silicates because the potential range accessible is approximately the same and limited by the same processes, namely, the formation of gaseous oxygen and platinum silicide at positive and negative potentials, respectively. Studies in borosilicate melts have concentrated on a composition suggested for the vitrification of nuclear waste ($57 \text{ SiO}_2 \cdot 12.2 \text{ B}_2\text{O}_3 \cdot 16.8 \text{ Na}_2\text{O} \cdot 11.1 \text{ Li}_2\text{O} \cdot 2.9 \text{ MgO} \cdot 0.2 \text{ ZrO}_2 \cdot 0.1 \text{ La}_2\text{O}_3$) [17]. Thanks to high alkali concentrations and, thus, to high ionic conductivities, measurements have been readily made as a function of temperature for a variety of polyvalent elements, transition metals included. The electrochemical series of elements is similar to that in a soda-lime-silicate glass melt, although the absolute values are somewhat different (compare [11, 17]).

By contrast, electrochemical measurements are difficult to perform in phosphate melts, probably because of high water concentrations. These lead to an increase in current at potentials more negative than 700°C , which is supposedly due to the formation of PH_3 or P_2H_6 . In a glass melt with the composition $\text{NaPO}_3 \cdot 2 \text{ Sr}(\text{PO}_3)_2$, an electrochemical series of elements has nonetheless been

determined. With respect to silicates, the main difference is that the redox pair $\text{Sb}^{3+}/\text{Sb}^{5+}$ has a standard potential that is more negative than that of the $\text{As}^{3+}/\text{As}^{5+}$ redox pair.

Future studies should also focus on polyvalent rare earth elements such as $\text{Ce}^{3+/4+}$, $\text{Eu}^{2+/3+}$, and $\text{Yb}^{2+/3+}$ relevant to luminescent materials (Chapter 6.3), which up to now have not been studied electrochemically. Here, the luminescence should widely be affected by the redox state.

Knowledge of thermodynamic data of redox equilibria is valuable to understand the redox reactions that are taking place when the temperature is changed. Although these reactions are frozen in below T_g , thermodynamics has indeed a stronger effect on these reactions than kinetics.

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5.10

Glass/Metal Interactions

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1 Introduction

Contact between metals and molten oxides takes place in a large variety of industrial processes. The resulting sticking and adhesion phenomena are either an integral component of the process or a drawback to be avoided. For example, preoxidation of a metal part ensures tight sealing with glass in fields as diverse as jewelry, decorative furniture, or electrical and electronic technologies. On the contrary, in glassmaking or glass forming (e.g. Chapter 1.5), sticking between the glass and the mold, crucible or stirrer must be avoided as it may induce defects on the product and corrosion of the tools.

The purpose of this chapter is thus to give an overview of the physicochemical interactions between glasses or melts and metallic materials. Complexity is actually a general feature of these chemical interactions because of the fundamentally different natures of metals and oxide melts. As metals and metallic alloys exhibit a high electropositivity, i.e. an ability to be oxidized to a cationic state, molten oxides are electrolytic solvents that may dissolve ionic species and in addition may act as oxidizing agents. Redox reactions involving dissolved metal and nonmetal species may thus occur in molten silicates and lead *in fine* to the dissolution of metallic solids if the metal and molten glass are in close contact over a wide interfacial area.

To deal with these interactions, the fundamentals of wettability and sticking will first be considered. Then the chemical interactions between glass and metallic alloys will be detailed as they rule the corroded or

passivated state of the metal. This done, the next three sections will be successively dedicated to the key parameters controlling the chemical reactivity of glass/metal interfaces, the methods and techniques used to study them, and finally typical cases of metallic materials corrosion.

2 Wetting, Sticking, and Adhesion Phenomena

Any study of glass/metal interactions must begin with wetting as it is the first step toward either the unwanted corrosion of the metal or the desired sticking and adhesion between the two phases [1]. Referring to recent contributions [2, 3] for a more detailed treatment and other examples, we will first state that the concept of wetting is based on the contact angle (Figure 1) measured between a glass droplet and the relevant substrate. In a first approximation, this angle is evaluated by the classical Young–Dupré equation, namely,

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cdot \cos(\theta), \quad (1)$$

where γ_{sv} is the solid surface energy, γ_{sl} the solid–liquid interfacial energy, and γ_{lv} the surface tension of the liquid in contact with the vapor phase.

Complete wetting consists in the total spread of the liquid onto the substrate, i.e. $\theta = 0$, whereas partial wetting is obtained for values of θ comprised between 0 and 90°. When wetting occurs it means, therefore, that γ_{sl} is lower than γ_{sv} , the difference ($\gamma_{sv} - \gamma_{sl}$) being its driving force. Many parameters influence the wetting of a molten glass onto a metallic substrate: (i) temperature; (ii) the chemical composition of the surrounding atmosphere, notably its oxygen fugacity; (iii) the roughness and composition of the solid surface, which can be oxidized or not; and

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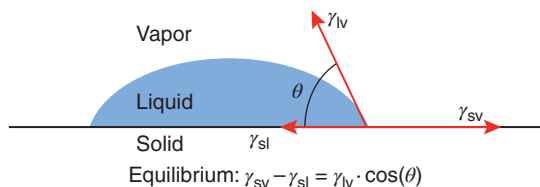


Figure 1 Scheme of a liquid sessile drop in equilibrium with a solid substrate: γ_{sv} is the solid's surface energy, γ_{sl} the solid-liquid interfacial energy, and γ_{lv} the surface tension of the liquid in contact with the vapor phase.

(iv) the composition of the glass, which determines both the rate of spreading and the potential extent of chemical reactions upon reactive wetting.

The wetting experiments made by the “transferred drop” version of the sessile drop technique proposed by Pech et al. [3] takes into account all these parameters (Figure 2). They are performed in a metallic furnace in an atmosphere of purified helium with an oxygen partial pressure lower than 10^{-9} Pa. The device must be equipped with windows so that the drop morphology can be video recorded at high temperature. The contact angle θ and the drop base radius R are then measured directly from the recorded images. The glass must first be introduced into the furnace on an auxiliary substrate. A dynamic vacuum is established ($P_{\text{total}} = 10^{-5}$ Pa), and the temperature is then increased up to 1200°C . This step allows gas bubbles to be removed and fining of the glass specimen to be achieved, typically in two hours. Then, the temperature is decreased down to the chosen wetting temperature (T_w) [3]. At this stage, the drop is raised until it touches the studied substrate to form

gradually a *pendular bridge* through which the melt is transferred to the substrate by capillary forces. Upon cooling, the last step consists in measuring the temperature at which the glass spontaneously separates from the substrate. This *detachment temperature* (T_d) is typically lower than the glass transition temperature (T_g) by several hundred degrees.

As an example, the wetting of a soda-lime glass – with 13.4 wt % Na_2O , 10.9 CaO, 1.4 MgO and 1.6 Al_2O_3 and $T_g = 560^\circ\text{C}$ – on a standard stainless steel substrate will be considered. The following observations are made [2]:

- The contact angle θ ranges from 60 to 70° between 965°C and 1200°C .
- The spreading rate increases with the test temperature.
- The substrate roughness increases the actual contact area and, therefore, causes a decrease of both the contact angle and spreading rate.
- The detachment temperature lies between 100°C and 150°C .
- The metal surface is not oxidized.

Interestingly, these results are not sensitive to changes in the contents of more (Cr, Si) or less (Ni, Co, Fe, Mo) oxidizable elements in the stainless steel. For a platinum substrate, a typical noble metal, the results are similar except for the detachment temperature T_d , which is just 20°C lower. Partial wetting is observed when metals are investigated in a neutral atmosphere. When electro-positive atoms are linked by metallic bonds, wetting is nonreactive and relatively insensitive to the nature of the metal. Adhesion is thus ensured by physical

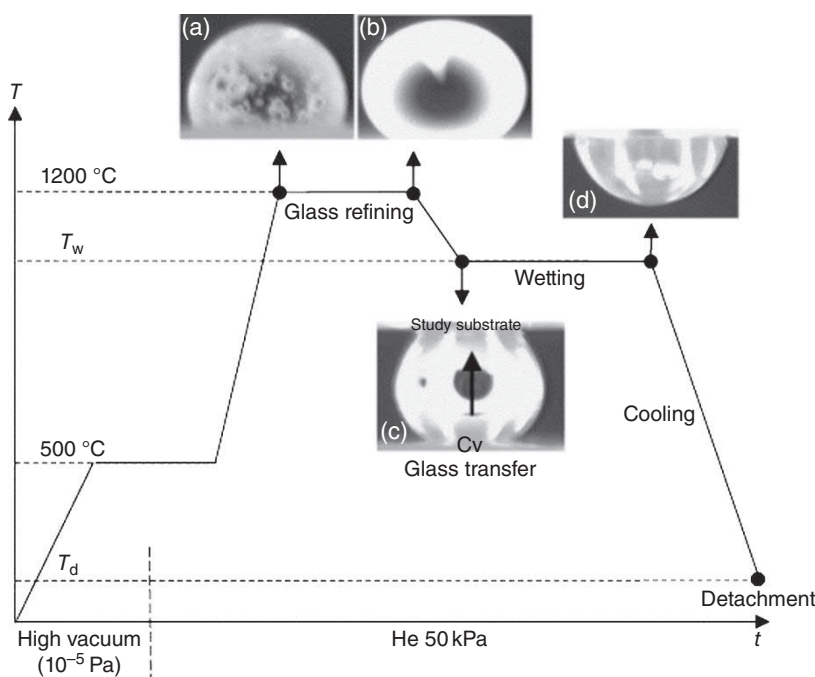


Figure 2 Successive temperature-time steps of the “transferred drop” variant of the sessile drop technique. (a) Deposition of the glass onto an auxiliary substrate, (b) glass after fining on the auxiliary substrate, (c) drop raised to the test substrate for transfer by capillary contact and formation of a pendular bridge, and (d) hanging glass drop. Source: Reprinted with permission from [3].

interactions. These results are consistent with those of Zackay et al. [4]. In contrast, for a vitreous carbon substrate, the contact angle θ and detachment temperature T_d are 135 and 300 °C, respectively. In such a non-electropositive compound characterized by covalent bonds, nonwetting is partial, and adhesion is rather due to van der Waals interactions and is thus relatively weak.

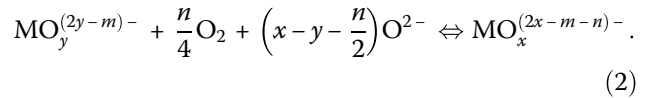
One can improve wetting and sticking by oxidizing the surface of the metal. The cohesion of the formed oxide is due to ionic (or ionocovalent) bonds. The same kind of bond can exist between the oxide and the glass, as the latter is also an ionocovalent compound. Under such conditions, low contact angles are actually measured with the transferred drop technique as a result of a reactive wetting process. In addition, good adhesion is achieved since no detachment is observed ($T_d < 20$ °C), especially when the mismatch between the thermal expansion coefficients of the metal substrate and of the glass is well accommodated by the interfacial oxide layer.

The oxide layer can be formed either at high temperatures in atmospheres with high oxygen contents or by *in situ* oxidation of the immersed metal surface by the oxidizing species initially present or added to the glass [3]. In such cases, the oxide layer is permanently stable if its constituting elements have reached their solubility limit in the molten glass (see Section 3). Clearly, these concentrations are determined by the overall composition of the considered glass matrix. In many cases, however, oxide dissolution in the glass is quicker than its formation at the metal surface [3] inducing corrosion of the metallic solid [5]. A preoxidation treatment of the substrate is then necessary. These various features have been taken into account for developing optimized glass/metal interfaces with noble metals like Pt or Au and, more frequently, with oxidizable metals such as Cu, Ag, Fe, Cr, Fe–Ni–Co (Kovar), Mo, W, Zr, and Ti and their respective oxides [6]. Of course, these are widely used in many applications like sealants for vacuum tubes, incandescent light bulbs, or tight channeling of fuel and oxygen in solid oxide fuel cells [7]. Other promising applications are self-healing materials such as glass–vanadium–boron composites as their oxidation leads to the formation of a $V_2O_5 \cdot B_2O_3$ glass ($T_{\text{melting}} = 700$ °C), which can wet, fill, and heal cracks during service.

3 Control of High-Temperature Chemical Interactions at the Metal/Molten Glass Interface

The chemical reactions occurring at the glass/metal interface are controlled by the chemistry of the melt and the reactivity of the metal with the melt species. Three parameters must be considered. These are (i) the oxygen pressure (pO_2) at the metal/glass melt interface,

which controls redox reactions; (ii) the glass basicity (aO^{2-}), which controls oxo-complexation; and (iii) the temperature, which controls kinetic effects and reactivity through the Gibbs free energy driving forces. These three parameters are not strictly independent. Most elements present in melts can, for instance, react with free O^{2-} ions to form oxo-complexes in a way that also depends on pO_2 , as indicated by the general equation that describes redox equilibrium between two different oxidation states of the same element [8, Chapter 5.6]):



Besides, the potential E is related to the Gibbs free energy ΔG through the relationship: $\Delta G = -nFE$, where F is the Faraday constant (i.e. 96 500 °C/mol) and E is determined from

$$E = E_0 + \frac{RT}{nF} \ln \left(\frac{MO_x^{(2x-m-n)-}}{MO_y^{(2y-m)-} \cdot O_2^{(n/4)} \cdot O^{2-(x-y-n/2)}} \right), \quad (3)$$

where E_0 is the potential at the appropriate standard state, R the gas constant, T the temperature, and n the number of electrons exchanged in the reaction.

For a fixed melt composition, the stability domain of the redox species is summarized on a redox potential scale [5]. The *electroactivity domain* of the solvent is defined by the upper and lower redox couples, which are generally O_2/O^{2-} and Si^{IV}/Si^0 for silicate melts (Figure 3). But the width of this window does in principle depend on melt composition. For example, a high concentration of lead oxide PbO (such as in crystal glass) narrows it on its cathodic side because of the reduction of PbO into metallic Pb (Figure 3).

The solubility of oxides in melts also strongly depends on the melt potential, as illustrated by the chromium solubility or the residual sulfur content [9, 10] curves determined for soda-lime-silicate melts (Figure 4). The variations of oxide solubilities with the redox state of the melt can also strongly influence (and control) the formation (or not) of solid species at the metal/glass interface.

The formation of a layer at the metal/glass interface is summarized by the flowchart of Figure 5. At the onset of the metal/glass contact, the chemical potentials of the relevant components differ in the two phases, which means that the interfacial zone is not in an equilibrium state. Redox reactions are a way to lower these chemical potential differences: either an element of the alloy is oxidized by another of the melt, which is reduced (Figure 5a), or an element of the melt is reduced at the metal/glass interface, followed by subsequent oxidation of an element of the alloy (Figure 5b), resulting in the formation at the

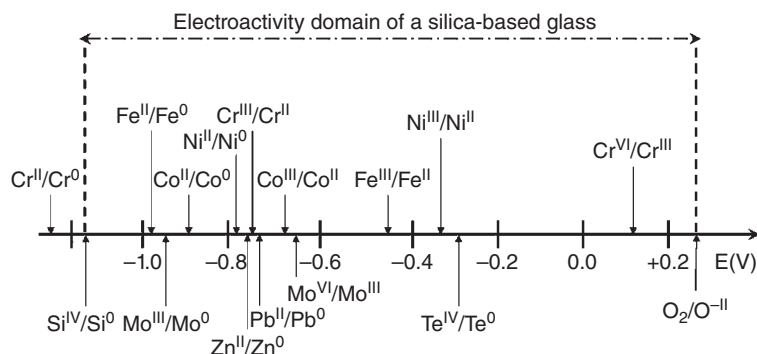


Figure 3 Scale of formal potential (E_f) at 1050 °C of the main redox couples present in glass or constituting alloys with reference to the yttria-stabilized zirconia (YSZ) electrode.

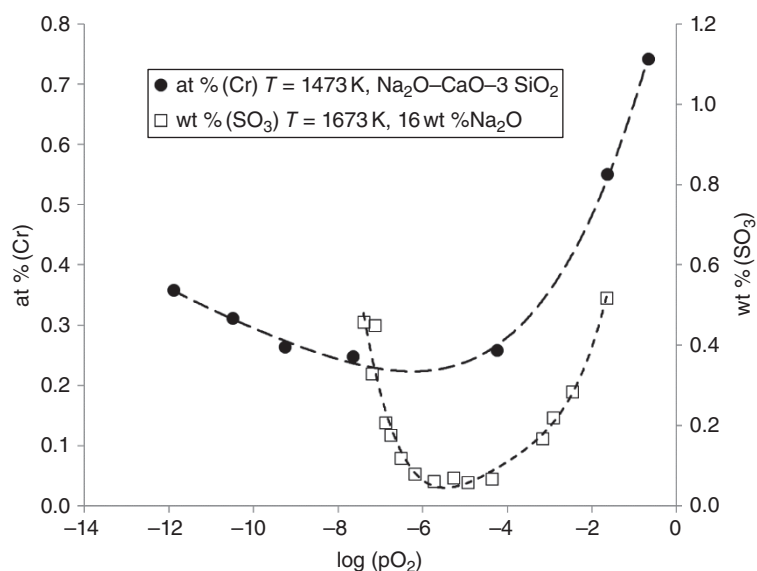


Figure 4 Chromium solubility (at %) and residual sulfur content (wt %) in a soda-lime-silicate melt versus oxygen partial pressure.

interface of an oxide layer and a metallic compound layer, respectively.

Depending on the species that form and on their reactivity with the elements of the melt, several reaction pathways must be considered:

- If an oxide layer forms, the oxide is stabilized at the interface when its solubility in the melt is low (Figure 5e), which limits the progress of the reaction. Alternatively, this oxide can react with elements of the melt to form another compound (Figure 5d). If the solubility of the oxide is high, it dissolves into the melt, which is then locally enriched with an element initially present in the alloy (Figure 5c).
- If a metallic layer forms, the metal can react with the alloy to yield intermetallic compounds through the solid-state (sometimes liquid-state) reactions determined by the phase diagrams (Figure 5f).

For the (c), (d), and (f) pathways, both composition (i.e. aO^{2-}) and melt potential are locally modified at the interface, and so do the chemical properties of the melt. The rate of these local modifications is directly related to the

temperature of the system. If it is very fast, the solvent properties at the interface can markedly change [11] and modify the initial reaction pathway, especially because the diffusion rate of O_2 in the melt strongly depends on the temperature. In addition, the equilibration of the chemical potentials at the metal/glass interface depends on the initial redox state of the glass and on the thickness of the melt layer between the metal and the surrounding atmosphere. Finally, the composition and physical state (solid, liquid, or gaseous) of the phase formed at the interface depend on temperature, so attention should also be paid to the pertinent phase diagrams.

4 Characterization of the Glass/Metal Interaction

Several experimental techniques and methods have been developed to study the formation of layers at the metal/glass interface either from *post mortem* analyses (i.e. qualitative and quantitative metallographic observations) or from *in situ* measurements (electrochemical studies)

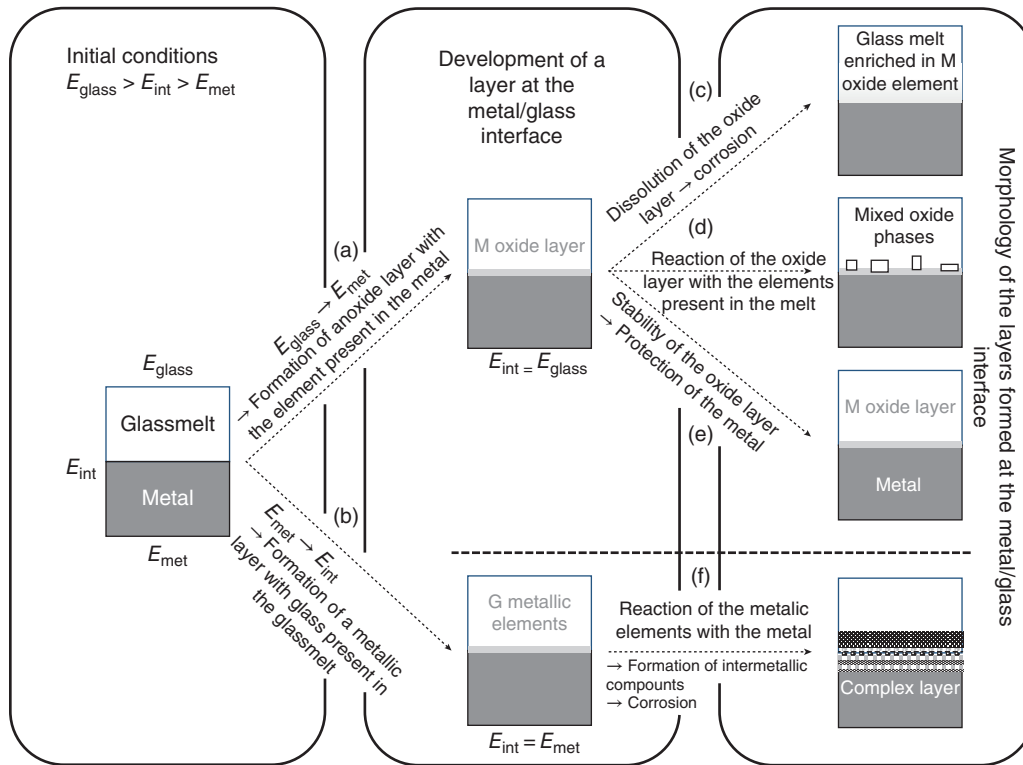


Figure 5 Pathway for the formation of layers at the metal/molten glass interface.

[8]. A combination of both methods obviously provides complementary information on the interaction mechanisms.

4.1 "Raw Immersion" Technique

An easy way to observe directly the influence of parameters such as glass composition, temperature, time of interaction, and surface state of an alloy (raw, preoxidized, roughness, etc.) on the reactivity of the alloy is provided by the "raw immersion" technique. With it, corrosion by a molten glass is carried out at a laboratory scale. A metallic sample is totally or partially immersed at high temperatures in a crucible filled with an appropriate amount of glass, the second configuration involving the presence of a triple point. After a given period of time, the sample is removed from the melt and quenched in air. A heat-shrinkable tube can be applied around the sample in order to preserve the glass surrounding the metal/alloy, which may crack upon quenching. All characterization methods of solids (scanning electron microscopy, electron probe microanalysis, etc.) can then be used to determine the morphology of the layers formed at the metal/glass interface and to investigate various features such as dissolution, reaction with the elements present in the melt, stability of the oxide layer, or reaction of the metallic elements with the metal. In addition,

corrosion rates can be determined from measurements of the thickness variations of the sample.

4.2 Electrochemical Methods

4.2.1 General Principles

As molten glasses exhibit a significant ionic conductivity, they are considered as good electrolytes. The use of electrochemical techniques is thus appropriate to characterize the various redox reactions involved in the corrosion of materials by these media. Because many such techniques may be used, only the most common in corrosion studies will be reviewed. Electrochemical measurements in molten glass are made in the same way as in aqueous media. The potential is controlled between working and reference electrodes, whereas the current density is measured between the working electrode and a counter electrode. Electrochemical measurements in molten glass require the use of specific materials that can withstand the harsh conditions imposed by high temperatures and contact with the molten silicate. Refractory ceramic materials (e.g. alumina, mullite, refractory cements) are recommended for constructing the electrodes, and noble metals such as platinum and Pt–Rh alloys are favored for the wires providing the electrical contacts.

The reference electrode must have a constant electrochemical potential in a given glass. Yttria-stabilized

zirconia (YSZ) is preferably used for this purpose thanks to its stability at high temperatures and to its high conductivity for O^{2-} ions that is at the root of the use of the redox couple O_2/O^{2-} as a reference. The counter electrode must be inert and present a maximum surface area to optimize current collection.

Depending on the nature of the study, two types of working electrodes are used. For characterization of glass properties, the working electrode also has to be chemically inert: noble metals are mostly used. For characterization of the metal/glass interaction, the electrode is made up of the studied metal in the form of a rod [5] or embedded in a ceramic tube letting a cross section serving as a surface electrode (Figure 6).

The nature of the crucible containing the glass is another important issue. A ceramic crucible is a low-cost solution. Its main disadvantages are brittleness, possible pollution by reaction with the glass sample, and the use for only one glass sample. A metallic (nonnoble) crucible is thus a better choice providing it is first subjected to polarization at a potential low enough to allow reduction of silicon, which will then be reoxidized into a protecting silica layer. As to noble metals, they suffer from their cost but have the dual advantage of high chemical stability and possible use as a reference and/or a counter electrode [11]. In this case, the existence of a triple point must be taken into account as it will cause a perturbation of cathode curves if gaseous oxygen is reduced into oxide ions in the melt.

When positioning the electrodes, the solution resistance must be minimized by keeping the tips of the electrodes as close as possible, especially for the reference and the working electrodes. The electrolyte resistance between these electrodes causes an ohmic drop that leads to an error in the measured potential differences. Molten glasses are most often highly conductive. It has been shown that an electrical resistivity lower than 4Ω has no influence on the measured potential differences.

4.2.2 Linear Voltammetry

With an inert working electrode, linear voltammetry is conveniently used to determine the electroactivity window of a glass. The same method can be used to study

the interaction of a metal with the same glass, the only difference being that the working electrode has then to be made from the metal in question. The existence of three domains can be demonstrated: active, passive, and transpassive (i.e. domain presenting corrosion phenomena at potentials higher than for the passive domain). Linear voltammetry is destructive since a large potential domain scanning modifies the surface state of the material.

4.2.3 Corrosion Potential and Polarization Resistance

The most basic electrochemical measurement is the corrosion potential (E_{corr}), which characterizes the active or passive state of the alloy and determines the reactions that may occur at the metal surface by comparison with the formal potentials of the redox couples (identified here with the standard potentials of the redox couples) present in the metal and in the glass. Experimentally, it is the open-circuit potential taken by a metal (i.e. the working electrode) under given conditions of temperature, glass and atmosphere compositions, etc.

The polarization resistance R_p is another important parameter, which can lead to the evaluation of the corrosion rate thanks to Stern–Geary method. Its measurement requires an additional counter electrode. A potential difference is applied between the working electrode (analyzed material) and the reference, as the counter electrode is used for current measurement. The working electrode is polarized around the corrosion potential (for example, from $E_{\text{corr}} - 10$ mV to $E_{\text{corr}} + 10$ mV). The calculation of the slope of the current vs. potential plot leads to the determination of R_p according to

$$\frac{1}{R_p} = \frac{di}{dE} \quad \text{at } E = E_{\text{corr}}, \quad (4)$$

where i is the current. By taking into account the number of electrons involved in the anodic and cathodic reactions, the kinetic parameters β_a and β_c are derived from

$$\beta_a = \frac{2.3RT}{\alpha_a nF}, \quad (5)$$

$$\beta_c = \frac{2.3RT}{\alpha_c nF}, \quad (6)$$

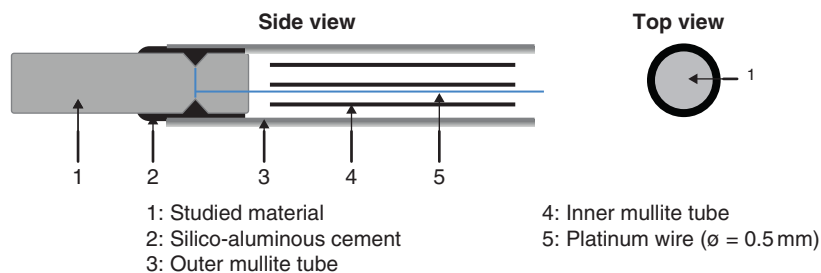


Figure 6 Sketch of a working electrode for corrosion characterization of metals and alloys.

Here n is the number of electrons involved and α_a and α_c are the charge transfer coefficients of the anodic and cathodic reactions, respectively (with values ranging from 0 to 1, which is generally taken equal to 0.5 in a first approximation). The corrosion current (which is directly proportional to the corrosion rate) is then obtained from the Stern–Geary relation

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \times \frac{1}{R_p} = \frac{B}{R_p}. \quad (7)$$

Finally an order of magnitude of the corrosion rate is given by Faraday's law

$$v_{\text{corr}} = \frac{I_{\text{corr}} t M}{n \rho F}, \quad (8)$$

where I_{corr} is the corrosion current (A/cm^2), t is time (s), M is the average molecular weight of the alloy (g/mol), and ρ is the average density (g/cm^3).

The measurement of both corrosion potential and polarization resistance as a function of time is an indicator of the evolution of the system. This technique is commonly used for the corrosion of superalloys by molten glasses. It allows the choice of adapted materials to be optimized under defined conditions according to their chemical composition, morphological properties, surface condition, etc.

4.2.4 Electrochemical Impedance Spectroscopy

Understanding the corrosion mechanisms and interpreting them in terms of diffusion, oxide layer formation, and charge transfer processes is another important goal. The electrochemical impedance spectroscopy (EIS) technique is well suited for this purpose, although few studies have yet been performed with it for molten glasses.

The impedance measurement can be performed under different conditions. The potential can be the natural potential of the alloy in the melt. Under these conditions, the alloy can be in active or passive state. As a consequence, interpretation of the impedance measurements must take into account the initial condition of the alloy surface. It is also possible to impose a potential, for example, to reach phenomena occurring when the alloy is in the transpassive state, at high potentials.

Much information can also be gained from Nyquist and Bode representations [12], i.e. plots of $-\text{Im}(Z)$ vs. $\text{Re}(Z)$ and of modulus and phase vs. $\log f$, respectively, on parameters such as the resistance of the electrolyte (R_e) or the charge transfer resistance (R_{ct}). The impedance loops (Nyquist representation) are attributed to charge transfer reactions in the alloy or in the formed layers, depending on their frequency range.

5 Corrosion of Metals and Alloys by Molten Glass

5.1 Corrosion of Pure Metals

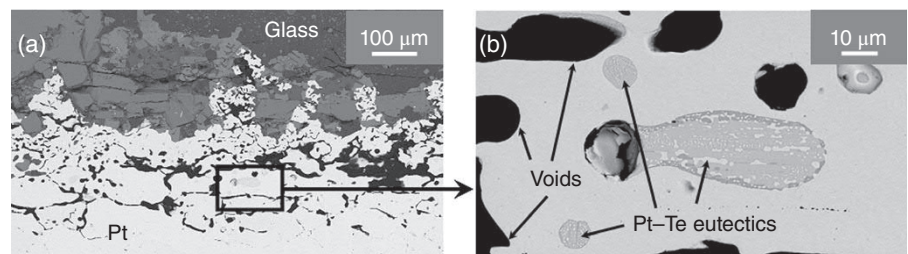
5.1.1 Noble Metals

To date, platinum and platinum alloys are extensively used in the glass industry thanks to their very high resistance to corrosion and erosion. Platinum is, for instance, used for melting pots, coating of melting vats, stirrers, and other ancillary equipment. Its high-temperature mechanical properties become limited above 1200°C , however, because of low creep resistance and recrystallization, which makes the penetration of the molten glass possible along the boundaries of the growing grains and, thus, causes degradation of the material.

Furthermore, Pt alloys can react in reducing atmospheres with metallic or semimetallic elements to form low melting point compounds [13]. Under reducing conditions, species such as Te^{IV} can be reduced to metallic state because the potential of the molten glass (-0.5 V) becomes lower than the formal potential of the $\text{Te}^{\text{IV}}/\text{Te}^0$ couple, namely, $E_f(\text{Te}^{\text{IV}}/\text{Te}) = -0.35\text{ V}$ (Figure 3). By reaction with platinum, tellurium then forms an alloy with a eutectic temperature lower than 900°C , thereby causing fast degradation of the material (Figure 7).

Platinum also undergoes catastrophic corrosion in a molten glass when it is coupled with other metallic substances such as nickel-based superalloys. Galvanic coupling not only increases the corrosion/oxidation of metallic alloys but also induces more damages in

Figure 7 Effects of tellurium reduction on platinum stability in argon atmosphere as seen on backscattered electrons micrography. (a) Pt sample immersed in a waste glass containing TeO_2 . (b) Higher magnification of the micrograph of Pt–Te eutectic grain boundary.



platinum. The reason is that, as described for reducing conditions, reduction of oxidized species of the glass (Si^{4+} , Mo^{6+} , P^{5+} , etc.) to a zero degree of oxidation takes place on the platinum surface where compounds with low melting points form.

5.1.2 Common Metals

Particular attention has been paid to Fe, Co, Ni, and Cr [5, 11] because of their presence in the cobalt or nickel-based superalloys mainly used in the glass industry. Their corrosion in a soda-lime-silicate glass has been studied with thickness-loss measurements and electrochemical methods. For Cr, the existence of a wide passivation plateau with very low current densities ($\sim 0.4 \text{ mA/cm}^2$) has been observed (Figure 8). The ability of Cr to build a protective chromia (Cr_2O_3) layer when imposing a potential lying in the passivation domain (from -900 to 0 mV according to Figure 8) demonstrates the possibility of using Cr as a protective component of superalloys in molten glasses. By contrast, the oxide layers that can form at the metal/glass interface with Fe, Co, and Ni are not protective.

When compared with thickness-loss measurements, electrochemical methods offer the possibility of identifying the corrosion mechanisms. This feature is of great importance since it opens the way to improving the corrosion resistance of metallic materials. In addition, the corrosion rates calculated from polarization curves are close to those determined from thickness-loss measurements [5]. Data obtained by electrochemical methods, therefore, can be used as semiquantitative indicators to classify metals and alloys according to their resistance against corrosion in molten glasses.

5.2 Corrosion of Alloys

In a hot corrosion context, Ni-based superalloys with a high Cr content and Al as an alloying element are a priori the best candidates for high-temperature applications (e.g. heating elements, gas turbine engines, etc.). The reason is that both metals have long been known to form at their surface the thermodynamically stable oxides Cr_2O_3 and Al_2O_3 .

5.2.1 Alumina-Forming Alloys

Corrosion of alumina-forming alloys in molten glasses is poorly documented in the literature. A recent study [14] has shown that upon raw immersion in molten glass, these alloys remain in the active state. An important Al loss is also observed. A preoxidation treatment does not improve the corrosion resistance. Indeed, according to the potential measurements, the alumina layer dissolves in the melt in a few minutes. This result is in accordance with the well-known high solubility of Al_2O_3 in oxide melts [15], which thus prevent alumina-forming alloys from being used as a high-temperature glass contact material (Figure 5c).

5.2.2 Chromia-Forming Alloys

In contrast, chromia-forming alloys are often used in the glass industry. As examples, they serve as construction materials for processing pots and susceptors in metallic melter pot furnaces, as well as electrodes in Joule-heated ceramic melter pots used for the elaboration of radioactive waste-containing glasses. Considering that the passive state can be obtained for pure chromium, similar studies have been devoted to chromia-forming alloys. For example, the corrosion of $\text{Ni}_x\text{-Cr}_{(1-x)}$ alloys, with $0 < x < 1$, in a soda-lime-silicate glass (with low MgO , Al_2O_3 , and Fe_2O_3 contents) is characterized at 1100°C

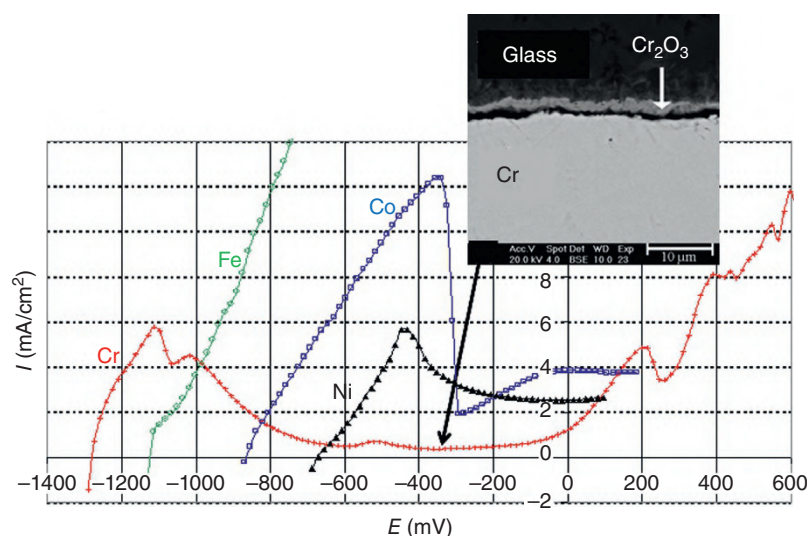


Figure 8 Passivation plateau of chromium seen in anode polarization measurements at 1050°C in an industrial soda-lime-silicate glass, contrasting with the sharp variation observed for iron, cobalt, and nickel. Inset: photomicrograph of the chromia protecting layer formed.

by important corrosion currents higher than 3 mA/cm^2 . A low Cr content in the alloy is not sufficient to build a protective oxide layer. On the contrary, a high Cr content induces spallation of the layer caused by the development of compressive stresses that result from the significant thickness of the forming chromia layer.

Di Martino et al. [5] have extensively studied the corrosion of Ni-based and Co-based commercial superalloys with chromium content as high as $\sim 30 \text{ wt } \%$ in borosilicate glass melts at 1050°C . Their results for a superalloy preoxidized or not immersed in the molten glass are compared in Figure 9. Direct immersion of the alloy spontaneously causes a corrosion that is characterized by a low potential (E_{corr}). When the alloy is in active state, the initial potential is low ($\approx -1.2 \text{ V}$, the oxidant being Si^{4+} ; Figure 3), and an anodic peak (here $I = 2.9 \text{ mA/cm}^2$) is followed by a wide passivation plateau with relatively low current densities ($I \approx 0.5 \text{ mA/cm}^2$). In the active state, the measured R_p values are close to $10 \Omega \text{ cm}^2$, which represents corrosion rates ranging between 15 and 35 mm/yr [5].

One can protect the Cr-containing alloys against active corrosion by performing a preoxidation treatment in air prior to the immersion of the alloy in molten glass (Figure 5e). This treatment “helps” the alloy to build a compact and adhesive chromia layer at the metal–melt interface that prevents direct contact between both phases. As a consequence, the alloy is directly in the passivation region characterized by a high corrosion potential ($-0.4 \text{ V} < E_{\text{corr}} < -0.1 \text{ V}$) and a high polarization resistance ($200 < R_p < 800 \Omega \text{ cm}^2$). These values point to

a corrosion rate of about 2 mm/yr, that is to say, one order of magnitude lower than that determined for an alloy in the active state. After several hours of immersion of a Ni–30Cr alloy in a silicate melt at 1050°C , a $3\text{--}5 \mu\text{m}$ thick chromia layer remains present at the metal/glass interface. This oxide layer is at the origin of the alloy passivation, preventing glass penetration and lowering the corrosion rate.

A 20–30 wt % Cr content in the alloy is thus required to develop a protective chromia layer. Nevertheless, depending on physicochemical conditions (temperature, melt composition, etc.), this chromia layer would not develop spontaneously in a molten glass, so a preoxidation step would be necessary to favor its formation at the metal/glass interface. Even though chromia-forming alloys show great potential since the solubility limit of chromia is one of the lowest among oxides [9, 14, 15], one must keep in mind that oxide growth always competes with dissolution in a molten glass: if the latter prevails over the former, the alloy will of course not be protected against glass corrosion.

5.3 Temperature Effects

These relative roles of oxide growth and dissolution depend on temperature. A transition from the passive to the active state of a Cr_2O_3 -forming alloy is shown by measurements of the electrochemical parameters E_{corr} and R_p as a function of the molten glass temperature [11]. At low temperatures, a chromia layer first develops at the metal/glass interface and ensures passivation of the

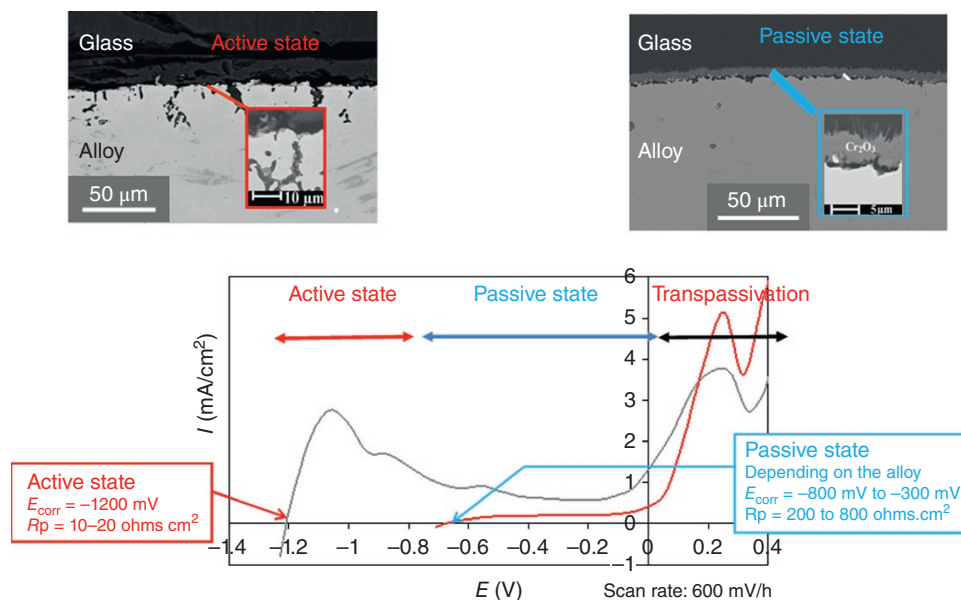


Figure 9 Anodic polarization curves of Co-based alloy in borosilicate glass for active and passive states at 1050°C . The interpretation of the curves is supported by the SEM micrographs for both conditions.

superalloy indicated by high E_{corr} and R_p values. With increasing temperatures, the alloy then proceeds to the active state upon drastic decreases of both R_p and E_{corr} . Whereas formation of the Cr_2O_3 layer is rate limited by diffusion of chromium from the metallic substrate and of dissolved oxygen from the molten glass, its dissolution is controlled by the solubility of Cr_2O_3 and the diffusion of Cr species in molten glass.

6 Perspectives

In any application, glass/metal interactions involve many individual processes. Studies of simplified systems will allow the effects of many physicochemical parameters (e.g. viscosity, basicity, etc.) to be determined individually. Likewise, the different elemental processes involved in corrosion mechanisms should be taken into account, and their kinetic contribution to the overall process should be estimated. Predicting the growth and dissolution of chromia layers as a function of temperature and alloy and melt compositions is, for instance, one of the main challenges for future developments. A predictive lifetime model could then be set up and applied to many applications, for example, the corrosion by CMAS-like glasses in aeronautical applications, the production of float glass, the sealing of solid oxide fuel cells stacks, etc. For this purpose, specific experimental and characterization methodologies need to be designed for each application. For corrosion by molten glass, electrochemical techniques are particularly adapted. They should be developed.

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5.11

Durability of Commercial-type Glasses

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1 Introduction

Chemical inertness is one of the key properties that has rendered glass so valuable two millennia ago when the invention of blowing made glass vessels of any size and shape commodity products in the Roman world (Chapter 10.3). As clearly shown by the marked iridescence commonly seen on ancient glass pieces, however, inertness was not absolute. Of course, one could rightly invoke the very long periods of time elapsed since their production to account for their superficial alteration. Under a variety of circumstances, it nonetheless happens that even modern products can suffer from an alteration strong enough as to make them valueless.

Problems caused by the reactivity of glass in wet environments are thus as old as glassmaking. They have long been rather well known, so industrial glass compositions have been optimized to satisfy many requirements, among them, the hydrolytic resistance needed for the intended use as exemplified by glasses used as containers in pharmacy (Chapter 7.7). As a rule, the problems stemming from glass alteration mainly occur instead under “unusual” storage or transportation conditions. Other corrosion occurrences are related to extreme conditions. Cases in point are those found in dishwashing machines where aqueous corrosion at relatively high temperatures may be favored by the detergents used together with rinsing and brightening agents.

In this chapter the basic alteration mechanisms in acidic and basic media will be first described. The specific problems raised by soda–lime, lead-crystal, or borosilicate glasses under their conditions of use will then be briefly mentioned. Next, attention will be paid to the

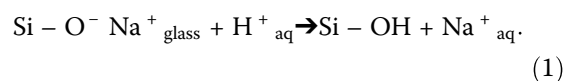
problems affecting flat and container glass during storage and transportation under confined conditions. Finally, solutions to this problem will be presented. By focusing on practical problems, this chapter may be considered as an introduction to the following one where corrosion mechanisms are reviewed in detail at the atomic scale.

2 Chemical Processes and Parameters

For all types of glasses, two chemical processes cause the initial modification of the material surface in contact with the aqueous solution. Their relative importance strongly depends on the pH of the medium [1–3].

2.1 Neutral or Acidic Media

In an acidic or neutral environment, a cation-exchange reaction takes place between network-modifying cations – sodium and calcium in soda-lime silicates – from the glass surface and the hydrated H^+ ions of the solution according to the reaction



With the exception of very pure vitreous silica, which lacks network-modifier cations, any glass exchanges ions as described by Eq. (1). This first reaction produces a hydrated dealkalized layer on the surface (Figure 1), usually called a *leached* layer, whose thickness is usually too small to affect the properties of the product. As an example, the dealkalized layer is about 100 nm thick in champagne bottles having been filled with wine for many years [4]. This thickness is nearly constant in the whole area in contact with the wine and indeed too small to compromise the properties of the bottles.

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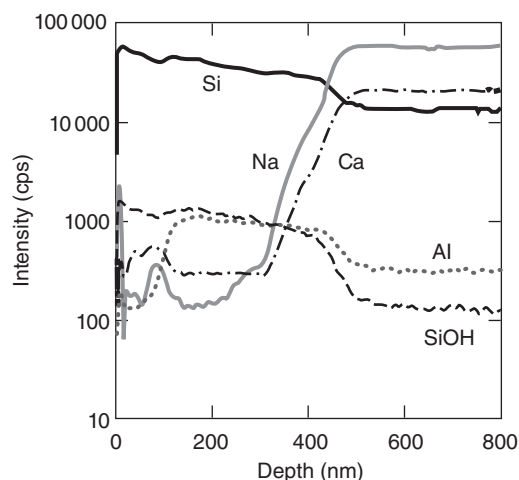


Figure 1 Cation exchange described by reaction (1) at the surface of a soda-lime silica glass as revealed by the contrast between the concentration profiles of SiOH and Na and Ca observed after water attack and rinsing.

The leached layer passivates in some way the glass surface as its presence decreases the rate of penetration of H^+_{aq} ions. Its growth kinetics (Figure 2) is typical of a diffusion-controlled mechanism because its thickness increases as the square root of time [5]. It is often described as a “gel layer” because its main component is SiO_2 -containing silanol groups SiOH. On the other hand, the high solubility of alkali cations in aqueous solutions makes them easy to be “missed” if the sample is rinsed before examination. Without rinsing either by the surrounding solution or by rain or any other external action, however, the alkali cations extracted from the glass are in general adsorbed or simply remain in the leached layer. As described below, this observation is consistent with reactions of the glass surface with atmospheric CO_2 or SO_2 .

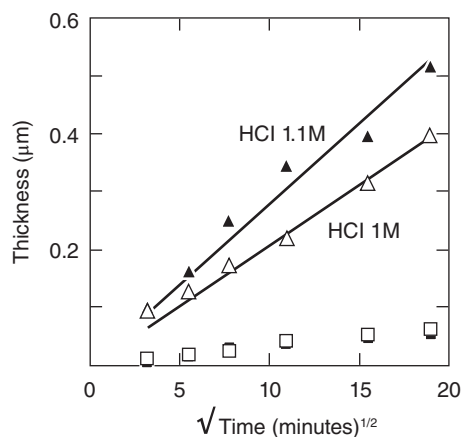
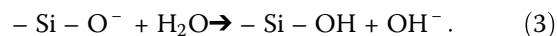
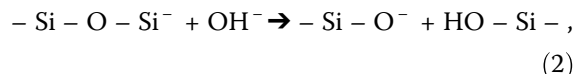


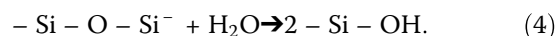
Figure 2 Diffusion-controlled nature of the alteration reaction (1) demonstrated by the linear relationship between the thickness of the leached layer and the square root of time (Source: From [5]).

2.2 Basic Media

In a basic environment, the alteration reactions are a little more complex because they involve the fragmentation of the silicate network and not a simple exchange of network-modifier cations:



Adding these two reactions, one describes the hydrolysis as



Reaction (4) takes place only when the pH is higher than 9 or 10 (Figure 3). It indicates that the OH^- ions are not consumed, but act as a catalyst causing the reaction to proceed linearly with time in the absence of the passivation layer that forms under acidic conditions (Figure 4). Then, the collapse of the silicate network can cause an irreversible alteration of the glass surface. Especially if it is spatially heterogeneous, this collapse modifies glass properties – optical, in particular – but sometimes mechanical as well. Owing to its intrinsically basic nature, cement, for instance, gives rise to an interaction with glass that is described in this manner [6].

2.3 Evolution of Water Attack: From Reactions (1) to (4)

The “basic” reaction (4) may also be considered as a continuation of the *acidic* reaction (1) because consumption of the H^+ ions of the initially neutral or slightly acidic solutions causes the pH increase required to trigger it. For this evolution to occur, however, the ratio between the area of reacting glass and the volume of the solution must of course be high. This condition excludes not only open systems but also glass immersed in a solution whose pH will very rarely become basic. Hence, it mainly applies

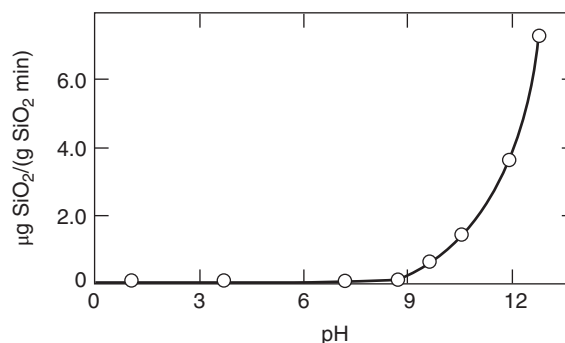


Figure 3 The very strong sensitivity to pH of the solubility of silica glass in an aqueous solution at 80 °C [1].

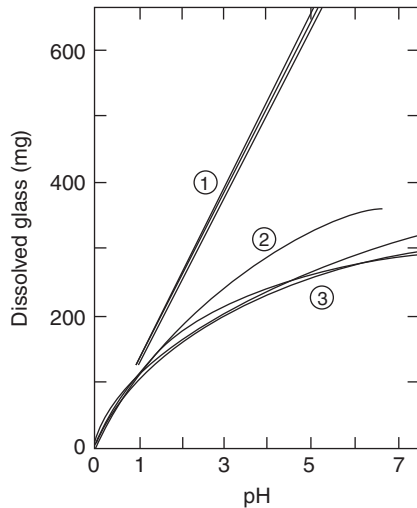


Figure 4 Effect of solution renewal on the dissolution kinetics of a soda-lime glass in a basic $N/2$ NaOH solution [3]: (1) 90 ml every 30 minutes; (2) 10 ml every four hours; (3) no renewal base line.

to products submitted to a confined, moist atmosphere such that the volume of water is actually small compared with the glass surface area.

As a matter of fact, after processing, the reaction can begin as soon as industrial products are submitted to a naturally wet atmosphere because the surface of alkali or alkaline earth aluminosilicates gets covered at room temperature by a very thin water layer at relative humidities as low as 30 % [7]. The process originates in the polar nature of the water molecule, which makes van der Waals bonding possible with a variety of high-energy surface defects such as low-coordinated charged silicons or isolated nonbridging oxygens. As a result of Eq. (1), the process yields OH groups on the surface, which are themselves covered with water molecules linked by van de Waals bonds. The water layer thickness depends on the partial pressure of water vapor (Figure 5). Even if water condensation is not visible on the glass surface, it follows that reactions between glass and water are nearly always possible. Museum rooms kept under controlled atmospheres are no exceptions.

3 Alteration as Related to Glass Composition

3.1 Soda-Lime Glass

Whether as flat, container, or even insulating fibers, glasses of the soda-lime family are by far the most commonly produced. Fundamentally their alteration originate in the relatively weak bonding of Na^+ ions to the silicate network as made obvious by the fact sodium-rich binary silicate glasses are highly hygroscopic: they would

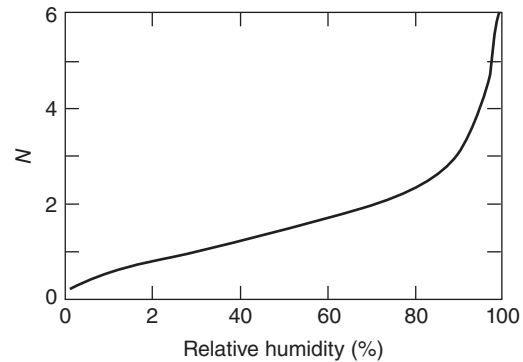


Figure 5 Average number of layers of molecular water on the surface of various glassy or crystalline oxide substances as a function of relative humidity [7].

simply disappear over rather short periods of time without the addition of calcium. But CaO is a poor flux compared with Na_2O , so increasing further the content of the less mobile Ca^{2+} ion to improve chemical durability [8] would end up in an enhanced devitrification tendency upon melt cooling.

Without this problem, in contrast, the introduction of 0.5–3 wt % Al_2O_3 in the composition notably increases glass durability [9]. Possibly a modification of the structure of the leached layer is involved, as suggested by Al_2O_3 contents that can reach 15 wt % in this surface layer. A second factor is the decrease of the content of network-modifier sodium ions resulting from their charge-compensating role for Al^{3+} in tetrahedral coordination (Chapter 2.4). At first sight such a decrease might seem too small to translate into significantly improved durability, but it is unlikely fortuitous that similarly small amounts of Al_2O_3 cause metastable immiscibility in the Na_2O-SiO_2 system to disappear [10]. One may thus surmise that introduction of small amounts of Al^{3+} results in a more homogeneous distribution of sodium in the overall structure, which makes H^+ ions less readily exchangeable for Na^+ .

3.2 Lead-Crystal Glass

At PbO contents higher than 24 wt %, lead-crystal glass presents a correct resistance to water hydrolysis, but it is more sensitive to corrosion in an acidic environment. Some lead can then be released in solution when drinking glasses and decanters contain liquids such as wine [11]. Regulating authorities have thus imposed leaching tests with a 4 % acetic acid solution for 24 hours at 22 °C [12] during which the amount of lead released must be lower than 5 and 2.5 mg/l for containers with a capacity of less and more than 600 ml, respectively. If the amount of lead released is greater than these values, either the composition of the glass must be modified to improve

its durability or the inner surface of the container must be treated to decrease the lead concentration in the first atomic layers so as to minimize further release upon use. The former procedure involves increases in SiO_2 , reduction of alkalis or addition of trace amounts of MgO or ZnO , and the latter acid polishing, ammonium sulfate fuming, or deposition of coatings [13]. That acid aging prior to use is an efficient manner to reduce subsequent lead leaching agrees with analyses performed on 24 % PbO lead glass decanters after 10 or 20 years of continuous use, which have confirmed that the process is self-limiting exponentially as a function of the distance from the glass–liquid interface [14]. This is the reason why crystal-glass manufacturers usually recommend to fill before use a new crystal-glass container with vinegar for 24 hours and then to rinse it thoroughly.

3.3 Borosilicate Glasses

Commercial alkaline borosilicate glasses (Pyrex® type) are well known for their high durability [15], which results from stabilization of alkali cations through charge compensation of tetrahedral boron (Chapter 7.6) and, in phase separated glasses, by the stable silica-rich matrix within which the phase rich in alkali borate is dispersed. The absence of alkali cations free to migrate into water from the surface yields a glass nearly as stable as silica glass, except in basic environments, which makes them in pharmacy the best containers for drugs (Chapter 7.7).

Other compositions of this type of glass are commonly used for vitrification of nuclear waste for very long-term storage (Chapter 9.10). In this particular case, the dissolution of the glass matrix nearly stops when the maximum solubility of silica in the surrounding medium is reached and a condensed protective layer forms. But this step is never encountered in common uses of ordinary commercial glasses.

3.4 Insulating Glass Fibers

With basically soda-lime compositions, to which a few wt% B_2O_3 are added, glass wool is closely related chemically to soda-lime silicate glass (Chapter 9.3). Its alteration thus conforms to the above description. The major difference concerns the extremely high specific surface area of glass wool. If these fibers are immersed into water, the pH immediately increases to values higher than 10.5 because of the very fast leaching of alkali cations made possible by the extremely high ratio between glass surface area and the volume of the solution. The attack may thus be very rapid if the product is not protected against water vapor condensation.

Insulating glass fibers called rock wool are more resistant because they contain large amounts of alumina and

less sodium oxide (Chapter 9.3). Nevertheless, their specific surface area is very similar, so potential problems related to the pH increase are only delayed.

3.5 Reinforcement Fiberglass

The typical E-glass used for those applications is a calcium aluminosilicate containing less than 1 wt % of Na_2O (Chapter 1.6). The sizing covering the fibers is in principle efficient against water penetration. Corrosion nonetheless can take place through interaction with acidic species that would be present in the immediate vicinity of the fibers. Calcium, aluminum, and boron are then extracted, potentially inducing a loss of mechanical properties.

4 Post-Production Corrosion of Flat and Container Glass

4.1 Flat Glass

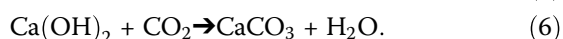
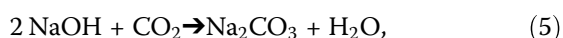
The composition of soda-lime glass has only changed marginally ever since it was produced at a really industrial scale two millennia ago in furnaces of up to 20-ton capacity (Chapter 10.3). Empirically, it had already been found that what we now term the eutectic region of the Na_2O – CaO – SiO_2 system was ensuring not only the lowest temperatures for melting and chemical homogenization but also the appropriate long-term durability with respect to rain and other atmospheric agents. Under usual climatic conditions, the thickness of leached-glass layer is smaller than 100 nm [16] because the corroding solution in contact with the glass surface keeps renewed, so the pH remains neutral.

In the modern world, however, this condition is not necessarily satisfied upon glass storage or transportation where efforts are made to save as much space (and air) as possible. For flat glass, the surfaces of the panels are, for instance, kept apart with *spacers*, usually polymer powders having a grain size of a few tens of microns. If water penetrates in between the panels, most frequently through condensation, then the ratio between the glass surface area and the volume of the aqueous solution can become very large, so the pH increases until reaction (4) begins. The leached layer has a different composition and, thus, a different refractive index. If its thickness reaches a fraction of 1 μm to become commensurable with the range of wavelengths of visible light, then iridescence will manifest itself as optical interferences. In addition, the attack cannot be homogeneous because water is trapped by the polymer spheres. The eye being very sensitive to optical differences, this inhomogeneous corrosion also becomes visible very rapidly through slight

light scattering. In this case, an acidic polymer may thus improve the situation.

In usual storage alteration, the chemical profile is characterized by a 100 nm-surface layer enriched in silica. Reprecipitation of silica extracted from the glass may yield a thin, very heterogeneous, and fragile, light-scattering layer on the surface. This type of defect appears faster when water condensation is coupled with high temperatures, for instance, upon shipping in tropical or equatorial areas. At a much smaller scale, the effect is similar to that observed on artifacts found in archeological excavations. This phenomenon also occurred in the early double-glazing windows within which air could circulate, but not fast enough to ensure a sufficiently low humidity content. The result was occasionally the formation of a whitish or even, in some extreme cases, crizzling layer.

When the surface modification is visible, the glass is usually rejected: Only polishing with cerium oxide could restore a satisfying surface, but the process is much too expensive to be applied to usual flat glass. Even if the modification has not yet become visible, the glass can still be useless for applications requiring treatments such as thin-layer deposition, a process commonly used today, because adhesion difficulties or problems caused by a heterogeneous aspect could occur. The precipitation of large crystals such as sodium and calcium carbonates or sulfates is less problematic when the species extracted from the surface (e.g. Na^+ , Ca^{2+}) and adsorbed in the “gel layer” react with gases present in trace amounts in the atmosphere such as CO_2 and SO_2 . For carbonates, these reactions are, for instance,



Usually those crystalline salts are simply washed out, with acidic water for calcium salts, before using the glass. Finally, a peculiarity of float glass (Chapter 1.4) should be

noted with respect to the asymmetry existing between the “tin” and “atmosphere” sides. The existence in the former of a sharp SnO_2 gradient beginning with contents of a few wt % right at the surface makes this side more durable than the latter, which in practice is the only one affected by corrosion.

4.2 Container Glass

After manufacturing, containers are gathered on pallets closed by polyethylene sheets and stored for periods typically ranging from a few days to a few months. Depending on storage conditions, water condensation can take place and cause alteration of the inner sides of containers according to reaction (1). Again, the extracted alkali and alkaline earth ions (in practice, Na and Ca) can react with atmospheric CO_2 to precipitate carbonates. Although SO_2 has a greater reactivity in this respect than CO_2 , the SO_2 partial pressure in the pallet is usually too low for sulfites or sulfates to precipitate.

Sodium carbonate crystals form as needles whose size reaches a few hundred microns, often well crystallized in a *crow's feet* pattern (Figure 6). They may be difficult to observe because a high hygroscopicity cause them to absorb so much water under a wet atmosphere that they dissolve in the form of a droplet, from which crystals can then reprecipitate under drier conditions. Owing to its small solubility of about 0.001 g/100 ml in water, calcium carbonate does not experience similar cycles of precipitation–dissolution. It forms instead small hexagonally shaped prisms that are initially about 1 μm long and become much larger when alteration proceeds (Figure 7).

Analyses of the glass underneath the altered zone or after light-acid washing shows that the glass surface is indeed depleted in Na and Ca. The optical aspect is slightly modified by a thin light-scattering layer that is not easily observed when the glass is colored. After

Figure 6 Effect of rinsing on the inner surface of a soda–lime bottle after a one-year outdoor storage as seen in SEM micrographs (2000 $\times$ magnification). (a) Before rinsing: presence of both Na_2CO_3 and CaCO_3 . (b) After rinsing: only CaCO_3 left.

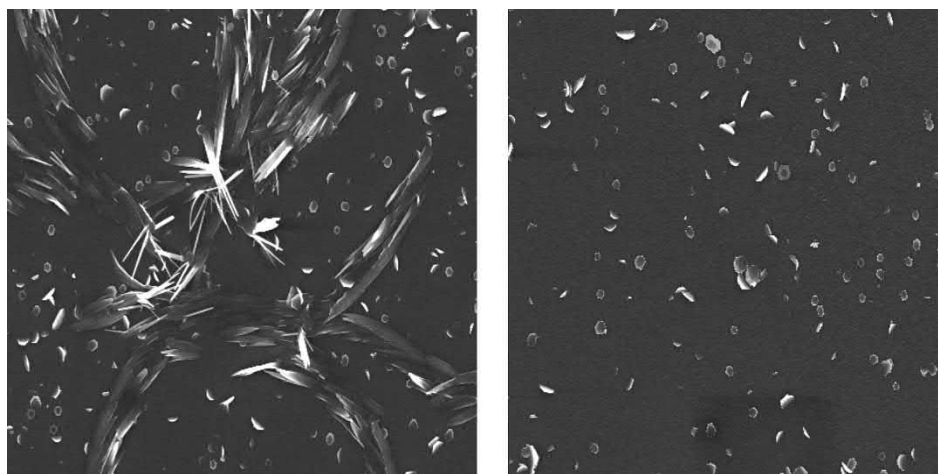




Figure 7 Optical micrography of large CaCO_3 crystal present on the inner side of a bottle stored one year without rinsing (magnification 200).

filling of the container, sodium and calcium salts dissolve because of the slight acidity of the content, and the veil thus completely disappears. But carbonate crystals can act as nucleation sites for bubble formation in the case of carbonated beverages, which then causes filling problems.

Under the adverse conditions, for instance, found in warm climates, one can observe below the CaCO_3 crystal holes of a similar dimension that signal a localized attack of the glass surface. As these crystals are especially insoluble, their presence as solid deposits on the surface can induce condensation of water if the relative humidity is high enough. The very basic pH locally induced by the process [17] generates defects that cannot be removed by an acidic treatment. This kind of extreme alteration was also observed when the first dishwashing machines used high-pH salts at high temperatures during long washing cycles. The attack was often nonuniform as a result of variations of chemical composition in the glass surface. As resulting from contact of the glass with the forehearth refractories, local Al enrichment leading to a reduced alteration could then be observed.

This type of chemical alteration can be found within containers but not on flat glass despite its lower hydrolytic resistance. This could be explained by the formation of sulfates on flat glass, instead of carbonates in bottle glass.

In the specific case of pharmaceutical bottles, besides the cations released, the porosity of the surface layer resulting of the attack can induce adsorption of molecules from the content on the internal wall of the container, thus the necessity of the treatment for this type of use (cf. Section 6). The external side can also present such phenomena, but the problem is less severe for two reasons. The first is that it does not have any consequence on the content of the container. The second is that this external side is usually covered with a thin protective tin (or titanium) oxide + polymer (PMMA) film (Chapter 1.5).

5 Characterization Methods

A brief summary of the various normalized tests devised to determine commercial glass durability is presented in Table 1. Apart from those normalized methods, other tests can be applied, especially to flat glass, in environmental climate chambers reproducing alternating humidity and temperature conditions. For practical purposes, a temperature increase of 10°C is considered to yield roughly a twofold increase of the alteration rate as a whole. This rule of thumb is of course approximate as reactions (1) and (4) have different activation energies, which should not be forgotten when corrosion tests are performed at temperatures higher than those of use to determine the durability of a glass. One must also keep in mind that the ratio between the surface area of the glass and the volume of the solution is the fundamental variable for the switch from reactions (1) to (4).

In addition to chemical analysis, it is essential to determine the species leached out of the glass surface after the test and to study the chemical modifications induced by the alteration. Various methods exist for such surface characterization, such as scanning electron microscopy,

Table 1 Summary of some tests made to determine glass durability.

Reference	Medium	Type of glass	Surface or bulk ^a	Temperature ($^\circ\text{C}$)	Time (hours)	Measurement
ISO 4802-1/2	Water	Any	Surface	121 (autoclave)	1	Acid/base, Na
ISO 720	Water	Any	Bulk	121 (autoclave)	1	Acid/base, Na
ISO719/DIN12111	Water	Any	Bulk	98		Acid/base, Na
ISO 7086	Acetic acid 4 %	Lead crystal	Surface	22	24	Pb, Cd, Cr

^a Bulk usually means that the glass sample is ground to a definite grain size so as to know accurately the surface area before testing.

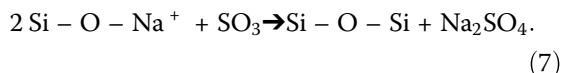
but mainly secondary ion mass spectrometry that allows concentration profiles to be measured with a resolution of a few nanometers (Chapter 2.3). When the attack is severe enough, the scattering of light observed in optical measurement can yield a good qualitative idea of the glass alterability.

6 Protection Methods

The most obvious way to protect flat or container glass against water corrosion is to keep it from variations of temperature and humidity during storage before use. But this is not always possible, especially for flat glass, which is subjected to longer travel times than containers whose rather low value makes long-distance transportation uneconomical.

Two solutions have thus been adopted by flat glass-makers, namely, deposition of a thin layer of a weak acid like adipic acid $[(CH_2)_4(COOH)_2]$; the precursor in nylon synthesis, which keeps the pH of the medium at low values; or pulverization at the surface of a Zn^{2+} -bearing solution. Although the actual mechanism by which the glass surface is protected by Zn^{2+} is not well understood, the effect results in a three- to fivefold time increase of safe storage.

For either pharmaceutical containers in contact with drugs or lead-crystal glass in potential contact with food or beverages, the hydrolytic resistance of the glass can be increased by up to 10 times if a dealkalization treatment is applied at high temperature. Referring to Chapter 7.7 for the former case, it will suffice here to state that several methods can be used [18]: dealkalization by ammonium sulfate, difluoroethane, or simply SO_3 . At high temperature (550–600 °C), sodium is extracted from glass and combines with the gas to give



On the surface of the glass, this reaction forms a few hundred-nanometer-thick layer, having a composition close to SiO_2 , which acts as barrier to sodium migration and block the advancement of reaction (1) at a negligible level.

7 Perspectives

Although modern industrial products do not often present visible alteration, glass is far from being chemically inert. It is not rare to observe modifications of its chemical composition within a surface layer of about 0.1 μm driven by the mobility of alkaline cations and their

exchange with protons coming from aqueous solutions. This modified layer is sufficient to make thin-film deposition difficult on flat glass, which has induced glass manufacturers to store newly produced pieces in controlled temperature shops and/or to reduce the storage time before coating, for instance, or making protection treatments, without completely eliminating the problem.

Modifications of the chemical composition of the glass through alumina addition has quite a large effect although this influence has not yet been completely explained. The probable reason is that Al_2O_3 accumulates at the surface in a hydrated form along with SiO_2 and so plays a role on the reorganization of the surface layer and on the diffusion processes through it. This layer being very rich in water, its examination under vacuum with usual analytical tools is not really adequate. As described in the following chapter, new methods are thus required to gain new insights on the chemical stability of glass.

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5.12

Mechanisms of Glass Corrosion by Aqueous Solutions

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1 Introduction

Chemical alteration by aqueous solutions is one of the most important processes undergone by glasses, either in industrial and environmental applications (Chapter 5.11) or naturally at the Earth's surface (Chapter 7.3). Induced by the intrinsic chemical instability of glass, aqueous alteration is referred to as corrosion in a laboratory setting, or chemical weathering in nature. Chemical weathering is due to the action of abiotic or biotic agents, or both, and plays a major role in controlling seawater chemistry and aqueous CO₂ uptake during dissolution [1], for example. Industrial and environmental applications of glass corrosion include the development of durable corrosion-resistant packaging (Chapter 7.7), in situ remediation of polluted water, carbon (CO₂) capture and storage, or secure, long-term isolation of industrial and nuclear waste (Chapters 9.9 and 9.10), [2]). Archaeometry is another important field associated with glass weathering and can be used for dating of archeological glass objects and paleoclimate reconstructions [3].

Knowledge of the molecular-scale mechanisms of alteration is a prerequisite for understanding how glasses react with aqueous solutions, thereby permitting more accurate modeling of corrosion and long-term durability. Corrosion is characterized by a combination of physical and chemical processes leading to the formation of one or more surface altered layers at the expense of the pristine glass. These layers not only are primarily composed of elements derived from the dissolution of the glass, but

also typically incorporate chemical species from the surrounding bulk solution. Separating the fresh glass from the solution, this near-surface zone has a varied terminology in the literature: leached layer, gel, surface altered layer, interfacial reprecipitate, palagonite. Because the phases making up this zone are intimately associated with the chemical alteration of the glass, understanding the details of their formation is crucial to elucidating corrosion mechanisms.

Two approaches are necessary to achieve this goal: the first aims at determining the chemical composition, structure, and physical properties (e.g. porosity, pore size distribution, permeability) of the surface altered layer(s), and the second at studying the interfacial region that delimits the boundary between the pristine glass and the adjacent surface altered layer. Critical to the development of a mechanistic model are accurate measurements of the chemical and structural gradients between these two phases. For this purpose, advanced analytical techniques having very high spatial resolution, elevated mass resolution, or both, should be used.

In this chapter, the discussion of corrosion mechanisms is largely based on a historical–chronological presentation. Two early models that characterized the state of knowledge up to the mid-1980s are first described [4], followed by the traditional model based on preferential cation leaching and interdiffusion. Frequently called the leached-layer model, it combines many of the elements found in the two early models. It has held sway over the past three decades and is still the predominant mechanism in the literature. The last model treated is relatively new and is based on CIDR. Acceptance of this mechanism, initially developed in mineralogy and geochemistry, has been quite contentious but has nevertheless been gaining attention in the glass community.

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List of Acronyms (cf. Chapters 2.3 and 5.1)

APT	atom probe tomography
EDX	energy-dispersive X-ray spectroscopy
CIDR	coupled interfacial dissolution-reprecipitation
EFTEM	energy filtered TEM
EPMA	electron-probe microanalysis
FIB	focused ion-beam milling
HAADF	high-angle annular dark field
HRTEM	high-resolution TEM
RBS	Rutherford backscattering spectrometry
RNRA	resonant nuclear reaction analysis
SIMS	secondary-ion mass spectrometry, including nano- and time-of-flight-SIMS
STEM	scanning TEM
XPS	X-ray photoelectron spectroscopy

2 Early Models

Dran and colleagues [4] summarized the two prevailing models regarding the aqueous dissolution of silicate glasses that held sway in the mid-1980s. The first was thought to apply to chemically complex or natural glasses. Its proponents postulated an overall congruent dissolution process, characterized by the stoichiometric release of both framework and network-modifying elements. As dissolution proceeds, the concentrations of silica and other elements build up in the bulk solution, so that upon reaching saturation, one or more secondary crystalline phases (generally silicates) precipitate onto the glass surface (Figure 1a). The alternate model was relevant to chemically simple, laboratory-produced glasses. It is based on the in situ preferential release of mobile,

network-modifying cations (e.g. Na^+ , Li^+ , K^+) into the bulk solution. Keeping the relict, leached glass structure electrically neutral requires replacement of the leached cations by H ions (most likely H_3O^+) from the bulk solution; this process may also be accompanied by the influx of molecular H_2O into the leached layer. The outer edge of the silica-rich leached layer releases Si and O to the bulk solution through chemical hydrolysis reactions (Figure 1b). Interestingly, one or the other mechanism has been used to account for the alteration of volcanic glasses, depending on their age [5].

3 Leached-layer Model

3.1 The Standard Model

The current generalized approach to glass corrosion has many similarities with the two early models. The altered zone, or leached layer, is composed of three separate entities (Figure 2). Adjacent to the pristine glass is an interdiffusion zone or layer, which is characterized by preferential removal of cations and sigmoidal chemical profiles, and is sometimes referred to as a hydrated glass layer [6]. Following this layer is a gel layer composed primarily of hydrated silica, where all the elemental concentrations are relatively constant. In the first stages of corrosion, the glass structure at the surface is progressively transformed by the selective leaching of certain cations (alkali and alkaline earth network modifiers, as well as network formers such as B) [2, 7–14]. For the interdiffusion zone to remain electroneutral, the preferentially released cations are replaced by H ions (i.e. H_3O^+) from the bulk solution. Each H_3O^+ -cation couple (e.g. $\text{H}_3\text{O}^+ - \text{Na}^+$, $\text{H}_3\text{O}^+ - \text{Ca}^{2+}$, $\text{H}_3\text{O}^+ - \text{B}^{4+}$) can be characterized by a single interdiffusion coefficient that depends

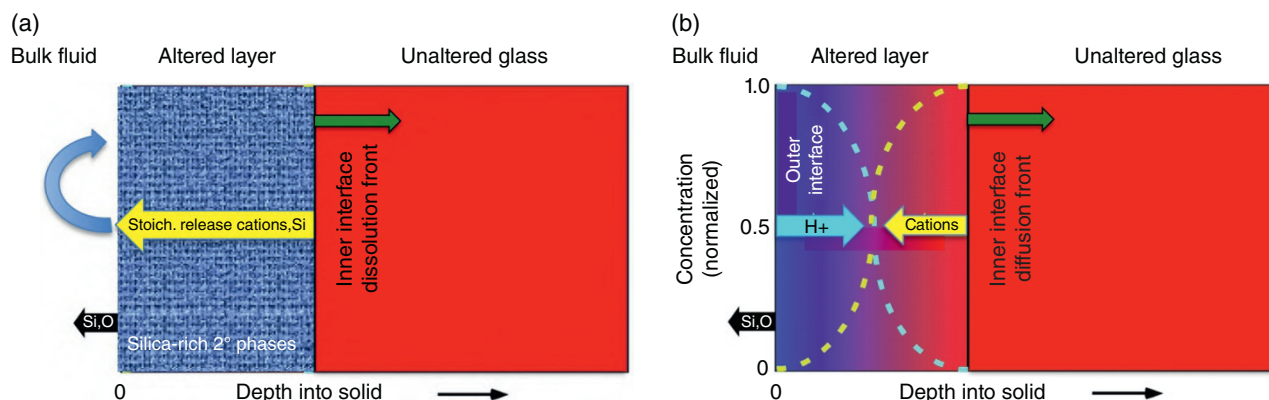


Figure 1 Cross-sectional diagrams of early models of an altered glass layer. (a) Congruent glass dissolution, followed by precipitation of secondary crystalline phases on the glass surface from a saturated solution. (b) In situ transformation of the glass structure via selective cation removal by interdiffusion, characterized by sigmoidal and anti-correlated H and cation depth profiles.

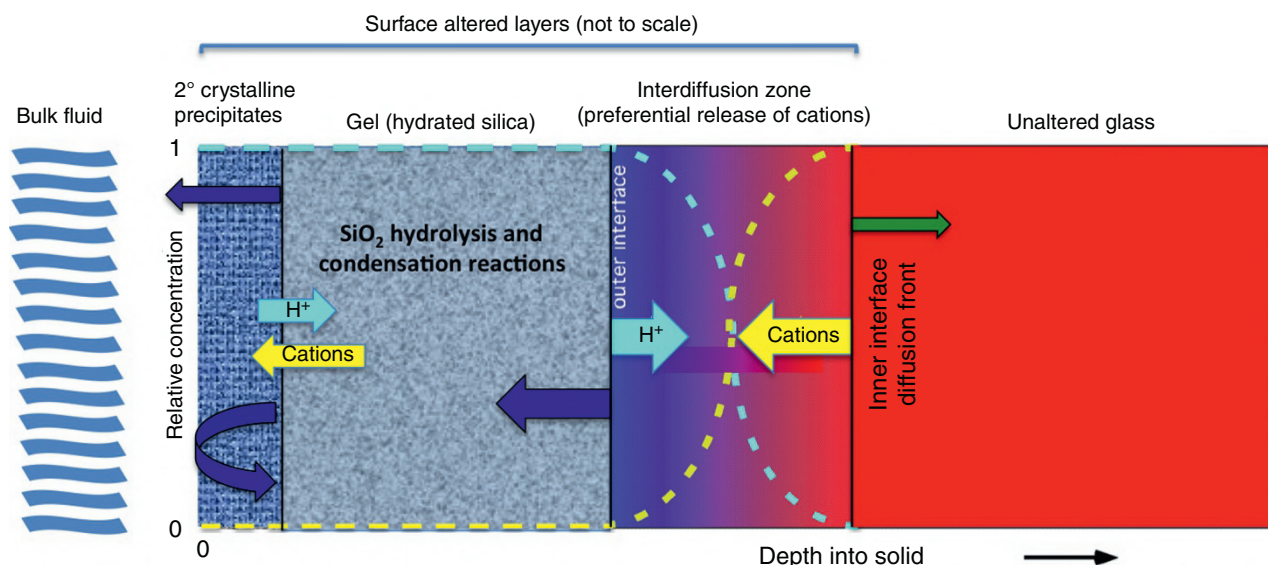


Figure 2 The distinct chemistry and structure of the three layers of the leached-layer mechanism: anti-correlated chemical profiles in the interdiffusion zone, relatively constant concentrations in the amorphous gel phase, and specific compositions of crystalline precipitates at the interface between the gel and the corroding aqueous solution.

on the individual diffusion coefficients of both components. In other words, the outward diffusion rates of cations are coupled to the rate-determining (slower) inward diffusion rates of H ions. For simplicity, only two profiles representing a single interdiffusion couple are shown in Figure 2, whereas in reality there will be multiple interdiffusion profiles with different gradients and depths, depending on the charge of the cation (i.e. interdiffusion of $\text{H}_3\text{O}^+ - \text{B}^{4+}$ will be significantly slower, and thus shallower, than $\text{H}_3\text{O}^+ - \text{Na}^+$).

Throughout the process, the inner interface of the diffusive layer (the diffusion front in Figure 2) continuously advances into the glass at a rate characteristic of solid-state volume interdiffusion. This process is the same as in the early model (Figure 1b), in particular because the leached relict zone remains covalently bonded to the pristine glass via Si–O linkages [7]. The outer interface of the diffusion layer is where silica is released to solution. Because of its relict nature and the sigmoidal shape of its diffusion profiles, the leached layer should not have a sharp structural and chemical interface with the pristine glass. At a significantly higher reaction progress (ξ), a separate porous gel layer composed primarily of hydrated silica begins to form on top of the diffusive layer, mainly by hydrolysis and condensation reactions. Hence, the diffusive zone advances by interdiffusion into the pristine glass at its inner interface and is consumed by gel formation at its external interface [2, 7–9, 14, 15].

Once the gel layer has formed and continues to grow, silica is released both at the outer interface of the interdiffusion layer, as well as at the external boundary of

the gel in contact with the bulk solution. However, silica resorption can occur throughout the gel layer when aqueous silica becomes saturated in the bulk solution and within the gel pores [2]. These processes are sketched in Figure 2 as (i) inward H ion diffusion, (ii) counterbalanced outward diffusion of preferentially released cations, (iii) silica release (straight dark arrows), and (iv) silica resorption (curved dark arrows). A net balance of all these rates governs the overall thicknesses of the interdiffusion and gel layers over time. The pronounced porosity of the gel layer allows for the unimpeded inward and outward flux of reactants and products between the bulk solution and the diffusive zone–pristine glass interface. In some cases, however, eventual pore closure in the gel layer may retard the overall corrosion process [16]. Moreover, depending on the composition of the glass, alteration conditions, and composition of the bulk solution, aggregates of secondary crystalline phases (zeolites, phyllosilicates, metal oxyhydroxides, hydrosilicates) may precipitate (Figure 2) on top of the gel as a third layer [2, 7–9, 15, 17].

The attributes of this model are well illustrated in a study [9] of the three-month aqueous alteration of SON68 borosilicate at pH 8 and 90 °C (Figure 3), a chemically complex analog of the glass produced at La Hague, France, for storing nuclear waste [7]. The three different layers illustrated in Figure 2 are apparent in the chemical depth profiles (Figure 3) determined by SIMS. The leached layer consists of an inner interdiffusion zone (where sigmoidal B and Li profiles are anti-correlated with a roughly sigmoidal H profile) and an outer gel (where

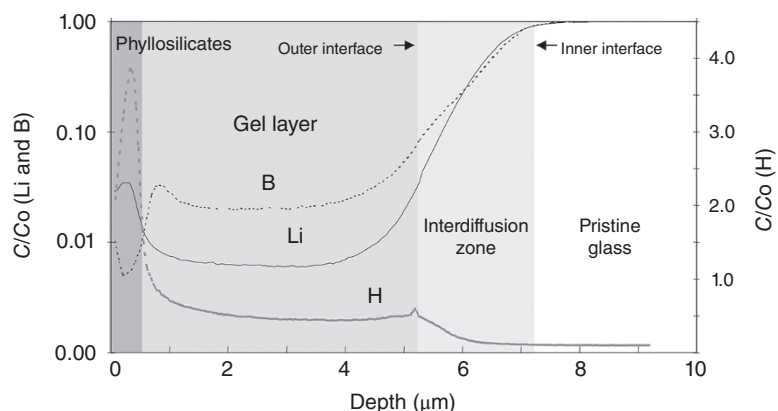


Figure 3 The interdiffusion zone, gel, and surficial crystalline phases of the leached-layer model illustrated by chemical profiles measured after a three-month corrosion of SON68 borosilicate glass at 90 °C and pH 8. SIMS O^- ion beam rastered over $250 \times 250 \mu m^2$ area, positive ions collected from window covering 60% of this area. Source: Adapted from figure 6, [9].

depleted B and Li and enriched H concentrations are relatively constant), on top of which phyllosilicates have crystallized as a porous layer. Currently, the leached layer model of glass corrosion, as exemplified by Figure 3, is the most widely accepted, in particular within the established glass community. It is the basis for nearly all codes modeling the macroscale chemical alteration of glasses in aqueous solutions (e.g. GRAAL [7]).

3.2 A Complex Hybrid Model

A major concern with most studies supporting the leached-layer mechanism is that the depths and gradients of the measured chemical profiles strongly depend on the analytical techniques used. This is illustrated by the results of a 25.75-year laboratory experiment [6], whose authors were among the first to study glass corrosion with atom probe tomography (APT), a very powerful technique that can provide three-dimensional reconstructions of the chemical and isotopic composition of a sample with subnanometer depth and lateral spatial resolution, as well as very high mass resolution ($m/\Delta m = 1000$, FWHM).

In this study, SON68 glass was altered at 90 °C and pH 7.0–7.2 in a slowly renewed granitic groundwater solution. From SEM observations, the sample consisted of the pristine glass, a hydrated (diffusive) glass layer (1000 nm), a gel layer (7500 nm), and surficial crystalline phases (a few hundreds of nanometer), yielding a total alteration thickness of approximately 9000 nm. High-resolution chemical profiles at the pristine glass-hydrated glass interface, determined by APT (Figure 4), reveal smooth decreases of Li, Na, B, and Al concentrations with increasing depth from the pristine glass interface, with gradient widths of ≈ 50 nm, and up to ≈ 100 nm for Na (Figure 4a). On the other hand, Si and H show smooth enrichment trends from the pristine glass interface, with gradient widths of 40–50 nm, whereas K (originating mainly from the granitic solution) and Ca increase over

distances of 10–20 nm and 100 nm. Much sharper gradient widths for Na and B (3–4 nm), K (5 nm), Li (17 nm), and H (20 nm) were also observed in this study (Figure 4b). Taken together, these results were interpreted in terms of a two-stage mechanism. First, an initial preferential loss of Li by interdiffusion with H occurred, which led to sigmoidal, anti-correlated Li and H profiles that became relatively constant after 15–20 nm. Subsequently, Na and B were preferentially released by dissolution, creating very sharp dissolution front profiles (Figure 4b), with strong depletion >15 nm depth.

In this hybrid model, an interdiffusion process has been combined with preferential dissolution, resulting in a steep interdiffusion front that is partially coincident in space with an even sharper dissolution front within the hydrated glass layer (Figure 5). The entire hydrated layer is by their definition a product of interdiffusion [6], but the results indicate that the diffusion profiles only extend to a depth of 20 nm from the interface with the pristine glass (Figure 4b). Diffusion modeling of leached layers [18, 19] shows that a 1000-nm thick diffusion zone characterized by a thin and steep diffusion front occupying only 20 nm at the inner extremity is physically not reasonable. In other words, the leached-layer model cannot explain how the remaining 980 nm of the hydrated layer forms, and in particular, why over the course of 25.75 years the Li and H profiles remained so sharp and so close to the interface with the pristine glass, although at the same time silica dissolution should have been occurring at the expense of the outer interface of the hydrated glass layer. Moreover, the K profile is anti-correlated with those of Na and B and mimics them in terms of sharpness and position with respect to the dissolution front. However, K had presumably diffused into the diffusive zone from the solution, a scenario that should have led to a K profile mimicking those of H and Li.

The suggestion of a hybrid diffusion–dissolution process occurring near the pristine glass interface is interesting, but whether this is physically realistic can be

Figure 4 Chemical profiles of pristine glass–hydrated glass interface obtained by APT of a borosilicate SON68 sample corroded 25.75 years at 90 °C and pH 7. (a) Profiles extending from the pristine glass to a depth of 500 nm into the hydrated glass. (b) Close up of the first 30 nm of the hydrated glass, based on original profiles (a) that were replotted with a “proximity histogram method”, producing significantly sharper elemental gradient widths. The true [B] may be lower than shown – see [6]. Source: Adapted from figure 3, [6].

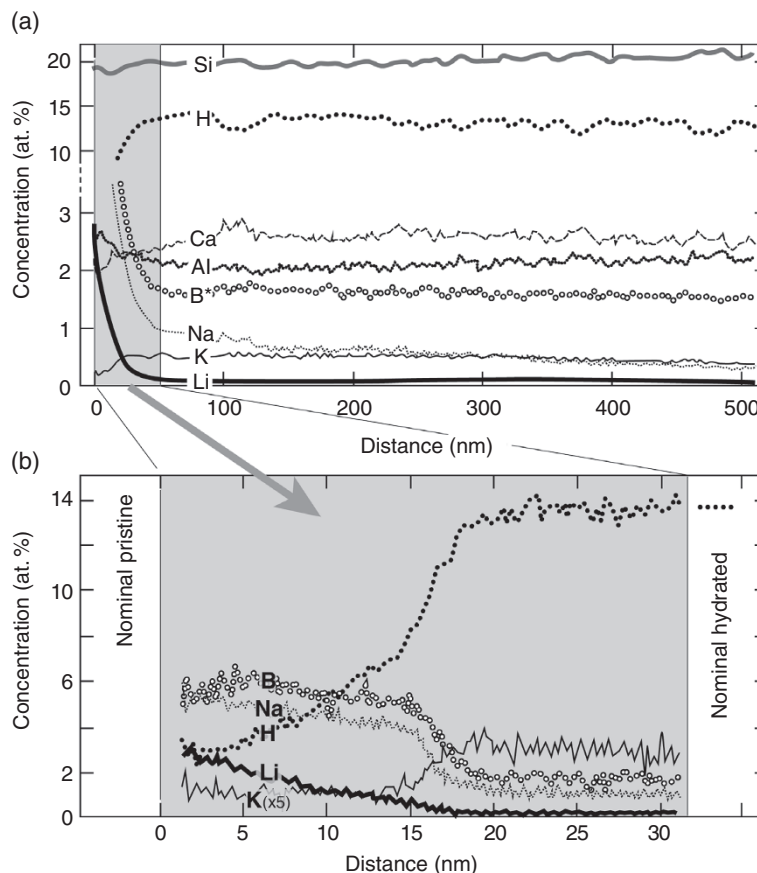
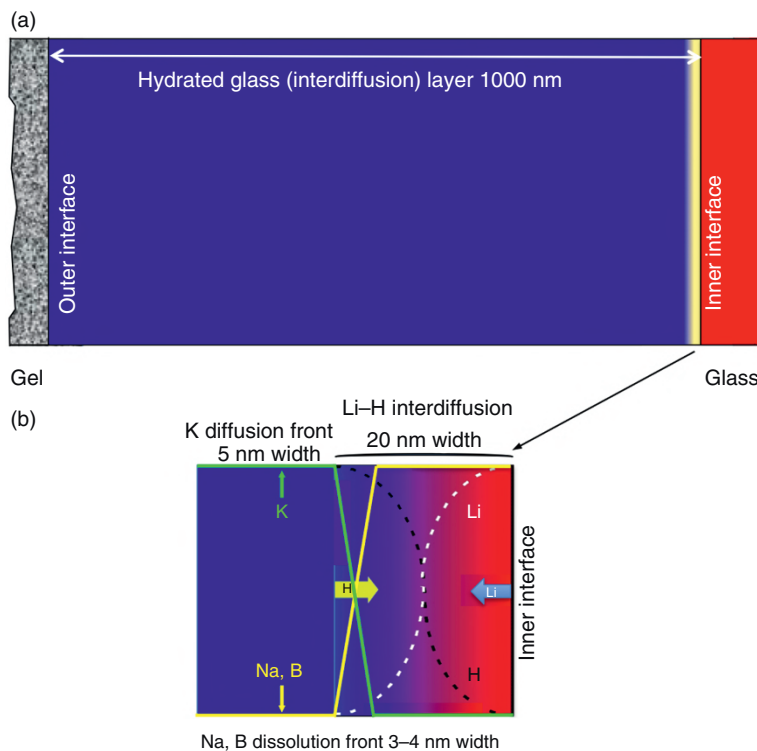


Figure 5 Hybrid leached-layer preferential dissolution model [6] illustrated by a schematic partial cross section of the hydrated layer and its two interfaces (refer to previous Figure 4). (a) The 1000-nm thick hydrated glass (interdiffusion) layer is shown in its entirety. The sharp interdiffusion profiles and preferential dissolution front occupy only the extremity of the hydrated glass layer, at the inner interface with the pristine glass (20-nm thick light vertical band, drawn to scale). (b) Close up of inner interfacial region, showing partially overlapping profiles representing interdiffusion (H and Li), preferential dissolution (Na, B), and diffusive uptake (K) from the bulk solution.



questioned. In particular, this process assumes that solid-state volume interdiffusion in a glass at 90 °C is faster than competing chemical hydrolysis reactions (e.g. [20]). If true, one could ask why the diffusion and dissolution fronts would still be nearly spatially commensurate after nearly 26 years in spite of their significantly different rates. The Li ion is small and carries a +1 charge, whereas the inward diffusing, charge-compensating H species (most likely H_3O^+) is significantly larger so that it will be much slower than Li and, thus, be rate determining in the Li–H diffusion couple [18, 19]. The ultimate question is, therefore, whether the Li and H profiles represent true interdiffusion, or an entirely different process. An alternative and physically more realistic explanation of the sharp chemical gradients measured, in particular for Li, Na, B, and K, is the coupled interfacial dissolution–reprecipitation mechanism.

4 Coupled Interfacial Dissolution-Reprecipitation (CIDR)

4.1 High-resolution Analyses

Regardless of the particular manner in which chemical profiles are theoretically interpreted, a fundamental point is that the need for high-resolution data is primordial. Two types of recent experimental and analytical advances fulfill this necessity. The first involves sample preparation techniques, initially ultramicrotomy [5, 15, 21, 22] and more recently, focused ion-beam (FIB) milling [23]. Not only have these techniques allowed altered mineral and glass specimens to be prepared in cross section, but the resultant ultrathin sections (lamellae) are electron transparent and, therefore, analyzable by TEM techniques. These advances have eliminated the need to use SIMS, XPS, RNRA, RBS, or EPMA to measure chemical depth profiles. These techniques are based on successive measurements starting from the top of the surface altered layer, proceeding downward through the layer, and finally finishing in the pristine mineral or glass. More importantly, their beam footprints range from tens of μm to several mm; when applied to samples with rough surfaces and irregular internal interfaces, the ensuing chemical profiles are artificially enlarged (i.e. smeared out), making them considerably wider than they really are.

The second important advance has been the use of analytical techniques having extremely high spatial resolution (Table 1), with beam footprints in the nanometer to sub-nanometer range, to measure surface altered layers directly in ultrathin electron transparent cross sections. These techniques, primarily TEM combined with electron-energy filtering (EFTEM) and electron-energy loss spectroscopy (EELS), or STEM-EDX (scanning

Table 1 Chemical-gradient widths (nm) of boron profiles in surface altered layers formed on SON68 borosilicate glass measured with different techniques [6].

ToF-SIMS	>1000
NanoSIMS (O^- beam)	350 ± 150
NanoSIMS (Cs^+ beam)	170 ± 30
EFTEM	≤ 30
APT	3–4

TEM-energy dispersive X-ray spectroscopy), have yielded novel nanometer-scale resolved chemical maps of the interfacial region encompassing the unaltered primary phase and the secondary surface altered layer(s). Moreover, high-resolution chemistry measurements of glass corrosion by TEM have recently been complemented by the application of APT, whereas isotope tracer experiments have provided unique insights into the dynamic nature of the corrosion process.

The power of these new approaches has been demonstrated by the nm-sharp chemical and structural interfaces evidenced in altered minerals (e.g. [19, 22, 24]) and glasses (e.g. [6, 16, 21, 25–27]). Spatially commensurate chemical and structural interfaces, which are very sharp at the nanometer to sub-nanometer scale, bear none of the hallmarks of diffusion, namely, smooth and broad sigmoidal chemical profiles spanning the region between the pristine glass interface and the outer boundary of the gel [18–20]. Likewise, the formation of rhythmic and patterned alteration layers with sharp chemical and isotopic boundaries reflect chemical self-organization processes that are difficult to reconcile with a preferential cation leaching–interdiffusion mechanism. In summary, techniques such as APT, EFTEM, and STEM-HAADF have allowed researchers to gain unprecedented chemical and structural data on interfaces needed to improve corrosion models, which have in fact contradicted the majority of previous studies on both mineral and glass alteration mechanisms.

4.2 Dissolution/Reprecipitation

Even though CIDR is a relatively recent theory as applied to glass corrosion, it traces its roots back to at least 1967, when it was proposed to explain the replacement of Na feldspar by K feldspar under hydrothermal conditions. Rather than invoking the standard idea of interdiffusional coupling of $\text{Na}_{\text{feldspar}}^+ \longleftrightarrow \text{K}_{\text{solution}}^+$ to explain the formation of authigenic K feldspar, O’Neil and Taylor [28] instead postulated that “the mechanism of oxygen and cation exchange in these experiments involves the fine-scale solution and redeposition in a fluid film at the interface

between the exchanged and unexchanged feldspar.” Hay and Iijima [29] perhaps alluded to a similar process, “The sharp interface between unaltered sideromelane [a basaltic glass, see Chapter 7.2] and palagonite suggests that palagonite was formed by a microsolution-precipitation mechanism rather than by simple hydration and devitrification.” In the following years, however, this new idea was to receive scant attention in the geosciences, or other related fields, for that matter.

Further development of the theory has been marked by an intertwined history between mineral and glass studies. At least 20 years ago, researchers primarily from the geochemical–mineralogical community began to question the fundamental tenets of the traditional leached-layer model when novel experimental/analytical approaches were developed and applied to altered samples. These led to new interfacial measurements that ultimately made this change in *status quo* thinking possible. Thus, it took about 30 years after the publication of the pioneering O’Neil and Taylor study [28] for CIDR to be resurrected and further developed into a more complete theory for both mineral alteration [22, 30] and glass corrosion [21, 25, 27].

According to the CIDR mechanism, the surface altered layer (i.e. equivalent to the interdiffusion zone and gel in Figure 2) is essentially a precipitate of amorphous hydrated silica. In a superficial sense, this model resembles that of Figure 1a, which is based on precipitation of crystalline (silicate) phases from an oversaturated bulk solution. The major difference is that the *coupled interfacial* dissolution–reprecipitation mechanism is based on an interfacial process involving tight spatial and temporal coupling between stoichiometric dissolution at a sharp chemical reaction front at the pristine glass surface, and quasi-simultaneous reprecipitation within an ultrathin fluid film in contact with the same interface. In cross section, this interfacial fluid film is composed of two to three layers of ordered water molecules (thickness <1.3 nm) whose physical, chemical, and rheological properties differ from those of bulk water [31, 32]. These differences are postulated to make the precipitation of a secondary silica-rich phase on the glass surface possible, even when the bulk solution is completely undersaturated with respect to all silica polymorphs (e.g. [25, 27]).

With the CIDR mechanism, glass corrosion is initiated by local chemical disequilibrium between the pristine glass surface and the ordered water molecules of an interfacial fluid film (Figure 6a), which results in hydrolysis reactions and the creation of a sharp dissolution front. The dissolution front is characterized by the stoichiometric release of the glass constituents into the fluid film. This process eventually leads to *interfacial* supersaturation within the fluid film, causing insoluble phases to precipitate (Figure 6b). Dissolution and reprecipitation are

nearly synchronous and spatially coupled within the interfacial fluid film. The predominant phase that generally precipitates is hydrated amorphous silica, but other insoluble metal oxyhydroxides (Fe, Al, Mo, etc.) may coprecipitate (at lesser concentrations) when these metals are present in the original glass structure. On the other hand, soluble cations, such as alkalis and alkaline earths, as well as boron, have only a minimal concentration in the reprecipitated layer through which they diffuse rapidly to the bulk fluid. In fact, the relative degree of retention of elements released from the glass structure in the altered layer is largely controlled by thermodynamics (i.e., by relative solubilities).

The thickness of the reprecipitated layer of silica increases with time and depends on the net balance between dissolution–(re)precipitation processes at both the outer and inner interfaces of the surface altered layer. Whereas the dynamics of the inner interface are controlled by the interfacial fluid, at the external interface they are controlled by the bulk fluid chemistry. An important aspect of the CIDR mechanism is that there is a net molar deficit for the overall reaction, which means that more moles of material are dissolved at the glass reaction front than are precipitated in the silica-rich surface altered layer. As a result, the reprecipitate is quite porous [30], which allows for the unimpeded inward and outward flux of chemical entities (dissolution products, water, and reactants from the bulk solution) between the reaction front at the glass surface and the bulk fluid. This is indicated in Figure 6b by the arrows connecting the bulk fluid with the interfacial film. The precipitation of loosely packed silica spherules in glass corrosion layers [26] is supporting evidence for intrinsically high porosity and permeability. Pore size modification or even closure within the altered layer can occur over time [16]. Porous aggregates of secondary crystalline phases (zeolites, hydrosilicates, phyllosilicates, metal oxyhydroxides [9, 15]) may also crystallize from the bulk fluid on top of the surface altered layer, depending on the glass, bulk fluid, and alteration conditions.

Perhaps, the most important characteristic of CIDR is that the structural and chemical interfaces between the pristine glass and the reprecipitated silica are both very sharp and spatially commensurate at the nanometer scale: in other words, they are the same interface. This would be expected for a precipitated phase in contact with an underlying parent phase. Evidence for such sharp and spatially coincident structural and chemical interfaces has recently been provided for a borosilicate glass altered in deionized water for four days and one, three, and seven months [27]. In a series of STEM-HAADF and EFTEM images (Figure 7), the surface altered layer grows in thickness with time, and the boundary between the altered layer and the pristine glass remains very sharp at the nm scale. In

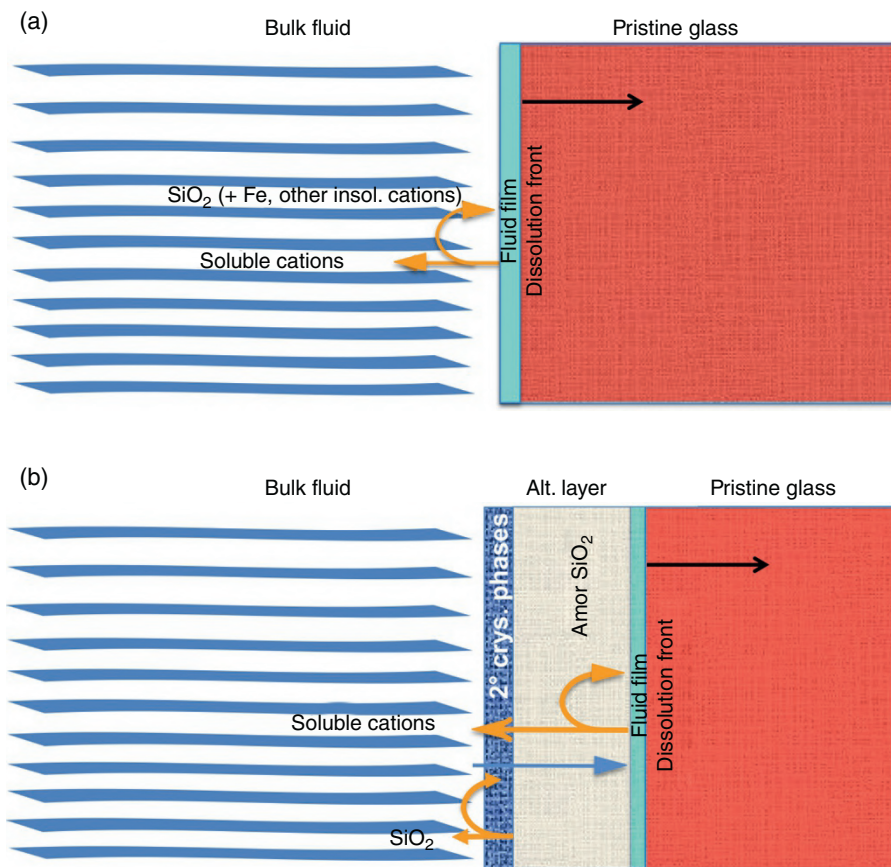


Figure 6 Glass corrosion by CIDR. (a) Initial stage: congruent glass dissolution in a thin fluid film comprised of 2-3 layers of ordered H_2O molecules. (b) Advanced stage: pristine glass, thin fluid film, reprecipitated layer primarily composed of hydrated amorphous silica, surficial secondary crystalline phases, and bulk solution. Soluble cations (B, alkalis and alkaline earth elements) diffuse unhindered to the bulk solution through the porous altered layer.

addition, the EFTEM chemical maps show that the altered layer is depleted in boron and enriched in silicon compared with the pristine glass and, most importantly, the chemical interface is also very sharp.

In that study [27], the one-month corroded glass was also analyzed by APT to obtain 3-D distributions of cations in the altered layer and in the pristine glass. In a 2-D view of two of these reconstructions (Figure 8a), the most interesting feature is the astounding sharpness of the chemical interface between the B- and Ca-depleted altered layer and the unaltered glass. The abrupt nature of the structural and chemical interfaces (Figures 7 and 8) is strong evidence in support of CIDR, but stands completely at odds with the leached-layer interdiffusion mechanism. Moreover, the depths of depletion or enrichment for seven cations measured by APT are all equal (≈ 50 nm, Figure 8b), even though these diverse cations carry charges ranging from +1 to +4. One of the tenets of diffusion is that cations diffuse at rates that vary inversely with charge (e.g. Chapter 4.3, and the diffusion profiles of Ref. [19]), but this is clearly violated by the results in [27]. It is also interesting to note that covalently bonded elements (network formers, e.g. Si, O, Al, B) and

more weakly bonded elements (network-modifying cations, e.g. Na, Li, Ca) show identical depths of depletion (Figure 8b), despite their fundamentally different structural roles in the glass. Taken together, these results refute a diffusion mechanism.

Other recent research also supports a nontraditional view of the corrosion process, or more precisely, the CIDR mechanism. In a recent isotope study [26], grains of a Na borosilicate glass enriched in ^{30}Si ($^{28}\text{Si}/^{30}\text{Si} = 5-8$) were altered in an aqueous solution in contact with a glass powder with a standard ratio of $^{28}\text{Si}/^{30}\text{Si} = 29.752$. A solution labeled with ^{18}O was used either for the entire experiment, or was added halfway through it. The resulting $^{18}\text{O}/^{16}\text{O}$ and $^{28}\text{Si}/^{30}\text{Si}$ isotopic profiles not only differ in the altered layer and the glass but also include rhythmic patterns and multiple peaks of enrichment as a function of depth (Figure 9). The Na profiles, on the other hand, revealed for the most part smooth depletion profiles, which might have resulted from the limited spatial resolution of the analyses. The textural interface between the surface altered layer and the pristine glass was sharp and characterized by chains of large pores. Finally, the altered layer showed evidence of spalling and flaking, indicative of very

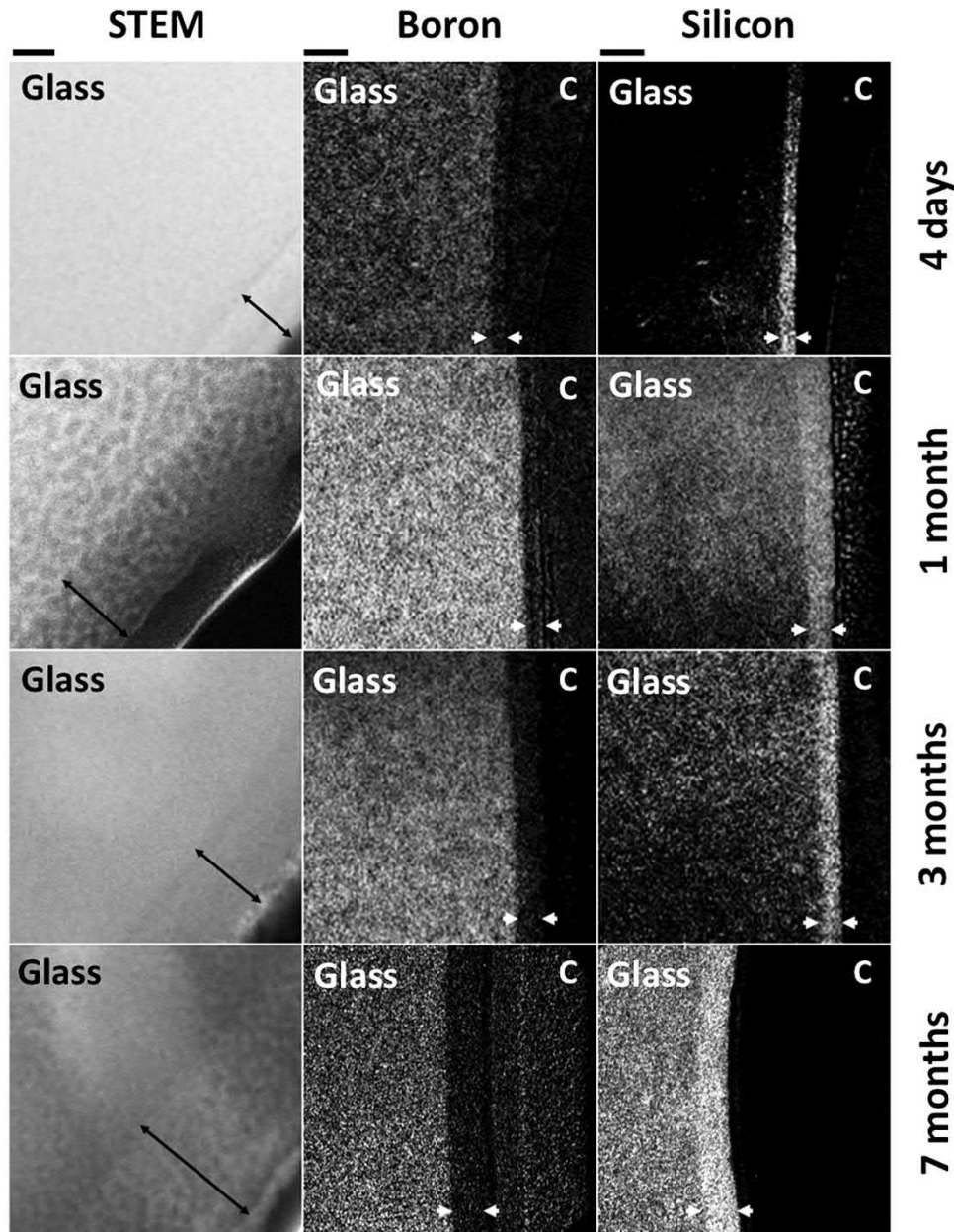


Figure 7 Corrosion of SON68 borosilicate glass altered at 50 °C in water for increasing periods of time. On left, STEM-HAADF images of the corrosion front, the surface altered layer is delimited by arrows (scale bar: 25 nm). Center and right: ETEM maps of boron and silicon, respectively, showing B depletion and Si enrichment (scale bar: 100 nm). In each panel, C denotes carbon (from sample preparation). Cross sections prepared either by FIB milling or Ar ion thinning. *Source:* Adapted from figure 1, [27].

weak adherence (i.e. bonding) to the pristine glass substrate – this would be expected for a mechanism based on reprecipitation. In an earlier study of borosilicate glass corrosion [25], the textural and chemical data were also completely at odds with the traditional mechanism in spite of the rather aggressive conditions of the experiments (initial pH $\approx$ 0, $T = 150$ °C). In the same study, a 2500-year old naturally altered glass from an archeological site revealed a

repetitive banding pattern in the corrosion rim, which quite closely resembles the chemical profiles obtained on the laboratory-altered glass [25].

4.3 Pending Questions

Recent evidence [25–27] strongly supports the CIDR mechanistic framework of glass corrosion, which is also

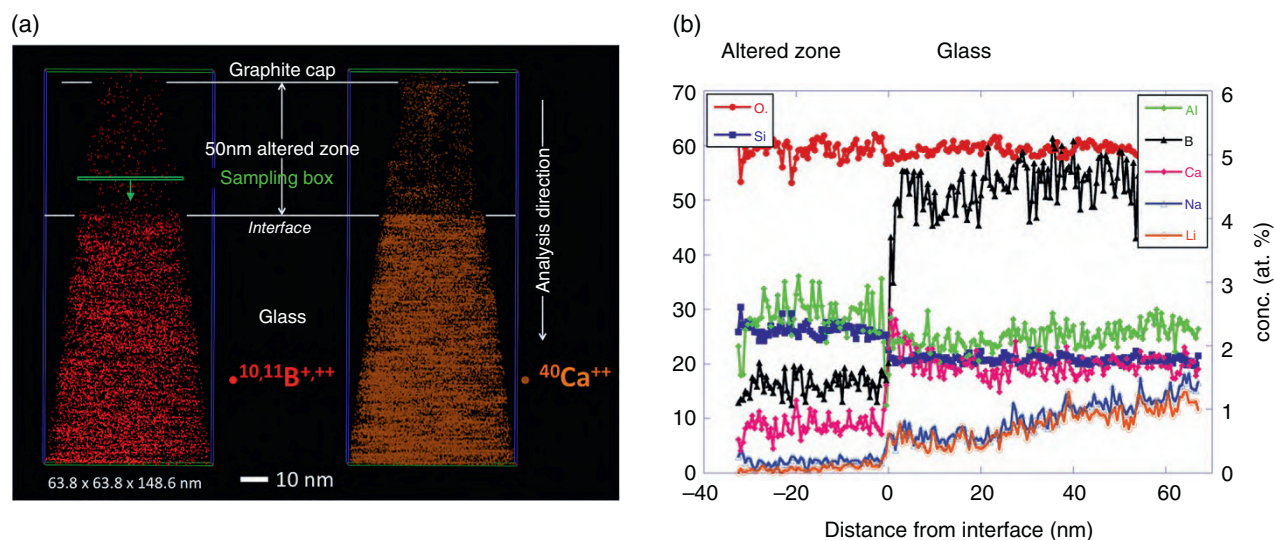


Figure 8 Chemical evolution of SON68 borosilicate glass after one month of corrosion measured by APT. (a) APT reconstruction of almost atomically sharp interface between the 50-nm thick B and Ca-depleted surface altered layer and unaltered glass (each dot represents an atom). (b) Chemical profiles across glass–altered layer interface based on 3-D APT reconstructions: note sharp concentration drops of B, Li, Ca, and Na and corresponding sharp increases in Si, Al, and O at interfacial boundary. Monotonous increases in Li and Na after initial jumps due to thermal diffusion during laser pulsing. Profiles at -20 nm, from high to low concentration: O, Si, Al, B, Ca, Na, Li. *Source:* From figure 2, [27].

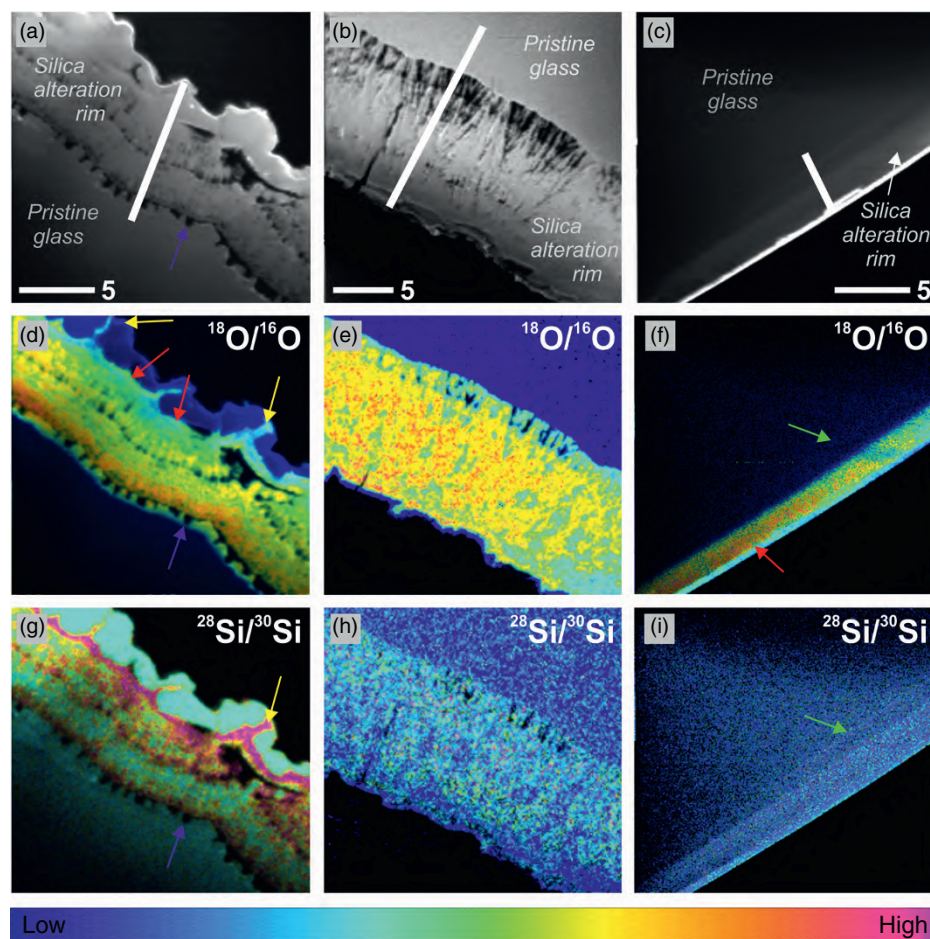


Figure 9 Complex chemical patterns and prevalent μm -sized porosity of silica-rich alteration layers formed during corrosion of a borosilicate glass: nanoSIMS intensity images of ^{16}O (a–c), $^{18}\text{O}/^{16}\text{O}$ (d–f), and $^{28}\text{Si}/^{30}\text{Si}$ (g–i) of glass grains enriched in ^{30}Si and reacted in ^{18}O -labeled solutions containing a glass powder with a standard $^{28}\text{Si}/^{30}\text{Si}$ ratio. Conditions: 672 hours, 90 °C, pH = 9.6. *Source:* Reprinted with permission: figure 3, [29].

consistent with the APT-measured chemical profiles in Figure 4a and b [6]. Nonetheless, the study of glass corrosion mechanisms remains controversial so that the CIDR mechanism is far from being universally accepted. One reason is the hypothesis of congruent dissolution at the glass surface reaction front; in particular, the idea that labile atoms, in particular network-modifier (or charge-compensating) cations, should be released at the same rate as covalently bonded framework-forming elements, which is perhaps counterintuitive. The CIDR model, however, does not exclude preferential ion exchange of cations with a fluid [22], as long as this process is restricted to labile atoms bonded at the *immediate* surface of the glass or mineral structure. The model does effectively preclude preferential ion exchange/release occurring deeper within the structure and the concomitant creation of a leached layer, which would invoke the (too) slow inward diffusion of reactants from the fluid. The exact mechanism of cation retention in the amorphous silica layer also merits more research. It is not known at present whether this occurs solely by coprecipitation with silica, or alternatively, by local precipitation of metal cation–oxyhydroxide phases within the nanopores of the silica layer. Cation adsorption on pore walls is another possible process. In fact, it is quite likely that all three processes occur during corrosion by CIDR.

The representation of a continuous fluid film contacting the pristine glass (Figure 6) may require refinement. This idea stems from numerous studies that have shown that altered layers are loosely bound, or even physically separated from the underlying glass [19, 26], resulting in facile detachment. On the other hand, not all studies have found evidence for spalling of the altered layer from the glass, suggesting stronger bonding. The interface might be more realistically characterized in terms of a dynamic island-fluid structure, as evidenced by chains of pores at the glass–altered layer interface [26]. Understanding the atomic nature of the interface and bonding between the altered layer and substrate glass, as well as the continuity of the fluid film, will require additional research. In particular, the use of aberration-corrected ultrahigh-resolution TEM applied to glass-altered layer interfaces may be one key to understand better how they evolve. Liquid-cell TEM (LCTEM) also shows promise as a frontier technique, as it makes possible the study of aqueous alteration of minerals and glasses *in situ* and in real time [33].

The above questions will need to be addressed in more detail in the future as CIDR is further refined. Whether or not CIDR is a universal corrosion mechanism also remains an open question, which can only be answered with more research based on cutting edge analytical techniques applied to new samples, or even to samples previously studied.

5 Rates of Dissolution and Element Release

5.1 Dissolution Rates and How They Are Measured

Aqueous dissolution data, and in particular dissolution rates, are a valuable complement to solid-state data in determining the mechanism of dissolution. The overall average long-term corrosion of glasses in aqueous fluids can be quantified in terms of total mass loss, normalized to surface area and elapsed time. However, in laboratory experiments, a far more useful quantification of corrosion is based on instantaneous rates of dissolution determined at specific time intervals. In a static reactor, the instantaneous release rate for any element i is defined as $R_i = dc_i/dt$ with units of $\text{moles}_{(i)} \text{m}^{-2} \text{s}^{-1}$. When a continuous flow-through reactor is used, the concentration of an element i measured at any given time is directly proportional to its release rate. Individual elemental release rates always need to be normalized with respect to the compositional stoichiometry of the pristine glass. Corrosion rates are commonly reported in terms of framework elements such as Si or B, depending on the type of glass undergoing corrosion.

The two mechanistic models presented in Parts 3 and 4 differ in terms of where Si release occurs. With respect to the leached-layer model, Si released to the bulk solution originates from the external interface of the gel layer and/or the diffusion zone (Figures 2 and 3). In the CIDR model, Si also has two possible sources: the fraction of Si released from the pristine glass within the thin fluid film that is not precipitated diffuses directly through the altered layer to the bulk solution; the other Si source is the external interface of the silica-rich altered layer in contact with the bulk solution (Figure 6b). In both models, the partitioning of Si release between their two respective sources is controlled in large part by the conditions of corrosion as well as the reaction progress variable.

5.2 Stoichiometry of Dissolution Rates

Glass dissolution kinetics can be quantified in terms of rates of release of network-forming cations, or alternatively, in terms of major elements present in the glass, irrespective of their structural role (i.e. network forming or modifying cations). The stoichiometry of glass corrosion is frequently reported in terms of individual cationic release rates. In acidic and circumneutral pH solutions, the normalized cation concentrations in the bulk solution are in general not equal (i.e. nonstoichiometric) when plotted as a function of time (Figure 10). Proponents of the leached-layer theory have used nonstoichiometric

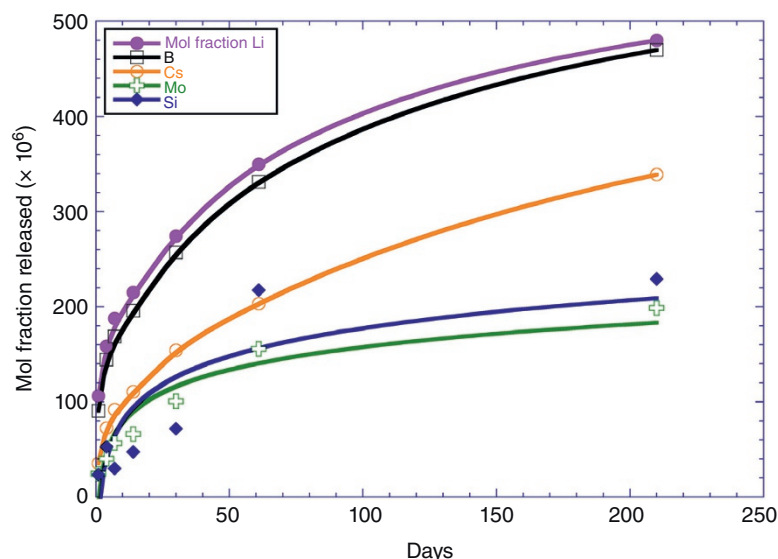


Figure 10 Aqueous elemental release curves as a function of time measured during corrosion of SON68 glass. The nonstoichiometry of the normalized elemental release rates ($R_{Li} \approx R_B > R_{Cs} > R_{Si} \approx R_{Mo}$) was attributed to solubility control (i.e. CIDR) within thin fluid film at pristine glass dissolution front. These data complement solid-state results for the one-month sample shown in Figures 7 and 8. Source: Adapted from figure S4, Supp. Information, [27].

release rates as evidence for preferential release of certain labile elements coupled to incorporation of hydronium ions from the bulk solution. This is manifested by higher apparent release rates compared with that of Si, which ultimately results in the creation of a relict Si-rich leached layer (Figures 1–3). However, the aqueous data purportedly showing preferential release can alternatively be explained in terms of CIDR. In this case the intrinsic dissolution process at the pristine glass surface is congruent, but subsequent retention (i.e. reprecipitation) of released elements is controlled by each cation's relative solubility in the interfacial fluid film. Thus, soluble cations (Li, B) are preferentially released to the bulk solution, elements such as Cs with intermediate solubility are partially retained, and finally, minimally soluble elements (Si, Mo) are preferentially retained by the precipitation of an amorphous silica phase. Thus, the composition of the altered layer can be estimated by thermodynamics. The strong correlation between relative elemental solubility [34] and degree of retention within the altered layer (Figure 10) is strong evidence in favor of CIDR and not an interdiffusion-controlled leached-layer process. This example also illustrates an important point: aqueous data alone, although useful, can be ambiguous and therefore do not lend themselves to precise mechanistic interpretations. Thus, obtaining nanometer-scale solid-state data is primordial for the determination of any corrosion mechanism at the molecular scale.

As a final note, the aqueous data shown in Figure 10 were used to calculate the Gibbs free energies (ΔG) of common low-temperature polymorphs of silica (Supp. Information [27]). All ΔG values were highly negative, thereby indicating that the observed amorphous Si-rich surface altered layers (Figures 7 and 8) did not precipitate

from an oversaturated bulk fluid, but more likely represent an interfacial reprecipitation phenomenon dependent on the special properties of thin fluid films.

5.3 Dissolution Rates as a Function of Composition

Chemical composition is major factor in the corrosion of glasses. A classification of corrosion resistance of a broad range of compositions and types [35, 36] shows the following generalized glass order (with some overlap between types): soda–lime (e.g. medieval and antique glasses) < nuclear high-level waste (e.g. SON68) < natural (e.g. obsidian) < commercial (e.g. Duran, Pyrex brands) < pure silica. A general rule of thumb is that corrosion durability increases with the proportion of network-forming elements (e.g. Si, Al, B) coupled to a concomitant decrease in the abundance of network-modifying elements (e.g. Ca, Na, Li, Mg, K). The former group of elements polymerizes the glass structure, whereas the latter depolymerizes it (Chapter 2.4).

To quantify these observations in terms of thermodynamics, many studies have used an approach based on a linear free energy relation (LFER). As developed in pioneering studies [37, 38], the LFER approach allows the susceptibility of glass to hydration (i.e. aqueous corrosion) to be estimated from the weighted sum of the Gibbs free energies of hydration ($\Delta G_{hydr(i)}$) of its individual orthosilicate or oxide constituents (i). Although based on some restrictions and simplifying assumptions [35], this approach offers a good starting point for qualitatively estimating the durability of a glass. Thus, species such as SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , and MnO_2 are predicted to stabilize the glass structure (positive ΔG_{hydr} values), whereas

CaSiO_3 , Na_2SiO_3 , and K_2SiO_3 destabilize it (negative ΔG_{hydr} values) [35]. There is, in fact, an inverse linear relation between $\log[\text{Si}]$ released and ΔG_{hydr} of the glass; in other words, the more negative ΔG_{hydr} , the less durable the glass and the higher the degree of Si release to solution. As a further refinement, ΔG_{hydr} can be adjusted for the solution pH to account for the dissociation of silicic and boric acids at high pH [36].

Glass composition is related to structure in terms of nonbonding oxygen (NBO) bonds, since ΔG_{hydr} correlates well with the number of NBO [37]. Hence, glass structure is usually not considered as a separate mesoscopic parameter distinct from composition. At the molecular scale it nonetheless plays a key role in glass corrosion, seemingly contradicting the preceding statement. As an example [16], it was found that the initial corrosion rate of a borosilicate glass was slowed down by substitution of zirconia (0–8 mol % ZrO_2) for silica. In the long term, however, the overall degree of corrosion increased with zirconia concentration because ZrO_2 hindered restructuring of the gel layer and, thereby, prevented pore closure. This phenomenon was deduced to be ultimately responsible for stopping corrosion by drastically decreasing the rates of diffusion of aqueous species within the gel.

5.4 Dissolution Rates as a Function of pH and Temperature

The effect of pH and temperature on glass dissolution is also quite strong and just as important as chemical composition of the glass. As has been developed and described in numerous geochemical studies for mineral dissolution kinetics, the following type of generalized rate equation for heterogeneous surface reactions [39] has also been widely applied to glass corrosion in aqueous solutions:

$$\text{Rate} = k_0 A e^{-E_a/RT} a_{\text{H}^+}^{n_{\text{H}^+}} \prod_i a_i^{n_i} f(\Delta G_r). \quad (1)$$

In Eq. (1), k_0 is the forward rate constant, A the reactive surface area, E_a the thermal activation energy of the overall reaction, R the gas constant, and $a_{\text{H}^+}^{n_{\text{H}^+}}$ the activity of H^+ raised to a power n ; the product operator term expresses the influence of the activities of other aqueous species that either catalyze or hinder the dissolution reaction; finally, $f(\Delta G_r)$ is a Gibbs free energy (or chemical affinity) term expressing the effect of deviation from chemical equilibrium on the rate, written here in a manner not based on any specific mechanism (e.g. transition state theory). By definition, $f(\Delta G_r) = 0$ at equilibrium. Many of the parameters in Eq. (1), such as k_0 , n , E_a , and $f(\Delta G_r)$, can vary as a function of temperature, pressure, pH, and other variables.

If corrosion takes place far from equilibrium and catalysis/inhibition due to other species in solution is unimportant, then Eq. (1) can be simplified and rewritten in terms of two equivalent expressions [39]:

$$\text{Rate} = k_0 A e^{-E_a/RT} a_{\text{H}^+}^{n_{\text{H}^+}} \quad (2a)$$

$$\text{Rate} = k_0 A e^{-E_a/RT} X_{\text{H}^+, \text{ads}}^{n_{\text{H}^+, \text{ads}}} \quad (2b)$$

Whereas Eq. (2a) expresses the pH dependence of corrosion in terms of the activity of H^+ , Eq. (2b) expresses it in terms of the mole fraction of H^+ adsorbed on surface sites. Both approaches are valid, but do not necessarily predict identical rates.

At any given temperature glass dissolution rates show the U- or V-shaped dependence on pH commonly observed for silicate minerals, which is not necessarily symmetric with respect to pH. As determined from regression of rate–pH data or adsorption isotherms of H^+ or OH^- , the values for n in Eqs. (1) and (2) generally range from 0 to 1 at acid pH and 0 to –1 at basic pH, where corrosion is catalyzed by H^+ and OH^- , respectively. At $4 < \text{pH} < 8$, the pH dependence is weak at most, so that corrosion rates are more or less constant (over a pH range that may be more restricted). Activation energies, derived from regression of $\ln R$ vs $1/T$ (K) data, are typically around 80 kJ/mol [34]. They are representative of hydrolysis reactions of 3-D networks of cation–oxygen framework bonds. With respect to both the leached-layer model and CIDR, an $E_a = 80$ kJ/mol increases the (Si) release rate by a factor of 20 between 25 and 55 °C. However, advance of the diffusion front into the pristine glass (Figure 2) is characterized by a significantly higher E_a , which reflects the extremely slow nature of solid-state diffusion at low to moderate temperatures [20].

5.5 Decrease of Dissolution Rates by Chemical Affinity (ΔG_r) and Pore Closure Effects

A smooth exponential decrease of release rates is observed in virtually all glass corrosion studies (Figure 10). In terms of leached-layer theory, this evolution has been split into five regimes [7] that have no precise boundaries: (i) initial diffusion (interdiffusion), (ii) initial rate, (iii) rate drop, (iv) residual rate, and (v) alteration resumption (only under certain conditions). The chemical and physical causes of the rate decrease have long been debated. In closed systems, a decrease of the $f(\Delta G_r)$ term in Eq. (1) has been commonly invoked as a result of the increasing concentration of dissolved glass species (i.e. Si) in solution. With the assumption of a rate-controlling activated-surface complex, Aagaard and Helgeson [40] calculated from transition state theory that:

$$f(\Delta G_r) = \left[1 - \exp \left(n \frac{\Delta G_r}{RT} \right) \right] \quad (3)$$

with $n = 1$ [39], Eq. (3) can then be expressed in a simpler form:

$$f(\Delta G_r) = (1 - Q/K). \quad (4)$$

Alternative relations have also been suggested, for instance

$$f(\Delta G_r) = \left(1 - (Q/K)^{1/n} \right) \quad (5)$$

with $n = 10$ [41]. In both Eqs. (4) and (5), Q refers to the ion activity product (IAP) of a given dissolution reaction, and K refers to the IAP at chemical equilibrium (i.e. solubility product).

Application of such relations to glass corrosion is problematic because a glass and a solution cannot be in chemical equilibrium since the reverse reaction will not lead to glass precipitation. Defining the Q/K ratio with respect to glass corrosion has thus been very controversial.

According to Grambow [42], dissolution of borosilicate glasses can be represented by the reaction $\text{SiO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$. This approach relies on the assumption $A_{\text{glass}} \approx A_{\text{SiO}_2}$ (A denotes affinity), such that the parameter Q in Eq. (4) represents the aqueous silica concentration in the bulk solution and porous gel, and K refers to the solubility of amorphous SiO_2 . At advanced reaction progress, the buildup of aqueous silica in the bulk solution and within the pores of the gel will progressively slow down the release of Si from the external interface of the diffusion layer (Figure 2). The original hypothesis of A_{SiO_2} -controlled dissolution was subsequently modified to include the effect of water diffusion through the hydrated diffusion layer [11]: if the layer is thin and water diffusion is unhindered, corrosion can continue at elevated rates, even for chemical affinity conditions of the bulk solution close to silica saturation. The same study [11] also suggested that soluble elements (e.g. Na and B) have a “collective response” with respect to silica concentrations, meaning that their release rates decrease significantly when the bulk solution attains silica saturation.

Nonetheless, the silica-affinity model [42] has been criticized for not being compatible with many experimental observations [8]. Recent experiments on SON68 glass based on progressive addition of aqueous silica (0–150 ppm Si) have also cast doubt on its validity [43]. Even though rates decreased by a factor of 150 upon addition of Si, their pronounced nonlinear nature stands at odds with the linear decrease predicted by Eq. (4). In part because of such observations, a similar affinity model depending on the dissolution affinity of the gel layer was proposed [44]. Rather than just considering silica, it postulates that all elements in the solution and in the

gel layer determine the dissolution affinity. This approach therefore predicts that long-term corrosion is controlled by the chemistry of the bulk solution, and in particular, by secondary phases, which precipitate and thereby control ion concentrations.

Another viable mechanism accounting for decreasing reaction rates is based on the transport properties of surface altered layers. These layers have the potential to decrease the bidirectional fluxes of aqueous reactant and product species between the bulk solution and the pristine glass. Alteration layers that form upon corrosion may be intrinsically dense, or may morphologically evolve with time so as to progressively decrease rates of diffusion of aqueous species within their porous structure. It has been argued that progressive densification of the outer parts of gel layers leads to pore closure [16], which in turn significantly decreases diffusion rates within the gel layer and thereby the intrinsic rate of glass dissolution. Another study used ^{29}Si isotope tracer profiles measured on two different sample faces after 86-day corrosion experiments [45]: from the outer gel edge to the gel–pristine glass interface, ^{29}Si diffused a total distance of 950 nm (bulk solution side); on the other side of the monolith in contact with a glass powder, the gel thickness was much thinner (≈ 150 nm), and most importantly, the gel acted as a diffusion barrier to ^{29}Si , allowing penetration only over the outermost 30 nm. For closure of gel porosity to occur, and by implication a corrosion rate that becomes negligible ($R \approx 0$), the authors [45] postulated that two conditions must be met: (i) the gel must have a high Si concentration, and (ii) the bulk solution must be silica saturated. Complementary Monte Carlo simulations supported these results and showed that clogging of the porous gel occurred at the external gel–bulk solution interface.

6 Perspectives

A systematic approach is needed to study in detail the molecular-scale mechanisms that control chemical alteration of glasses in aqueous solutions. This goal can only be achieved with a methodology that goes beyond standard analytical methods that have been widely used in the past. The choice of how altered glass samples are prepared, and which analytical techniques are used, is of critical importance for obtaining data useful in deciphering the molecular-scale mechanism of alteration, as well as modeling the glass corrosion process and its kinetics. Based on published data, the decrease in long-term rates of dissolution most likely are due to chemical and physical processes working in tandem. More in-depth work will have to be done to ascertain the partitioning between

chemical and physical rate-decreasing processes as a function of time during glass corrosion.

The cornerstone for the long-term prediction of glass corrosion is an accurate understanding of the underlying mechanism(s). Therefore, employing high spatial and high mass resolution techniques to analyze surface altered phases and their interfaces with unaltered glass should be strongly encouraged for future glass studies. Moreover, corrosion experiments using isotopically labeled bulk fluids, and in some cases even labeled glasses, have already shown their enormous potential to provide complementary information on the dynamics of glass corrosion. When taken together, the combined use of all of these advanced techniques may allow for a long-term goal to be realized: establishing whether or not all glasses are ultimately controlled by the same mechanism of dissolution. Going even further, it may perhaps even lead to a universal mechanism that links mineral and glass alteration processes at the nanometer scale.

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Section VI. Glass and Light

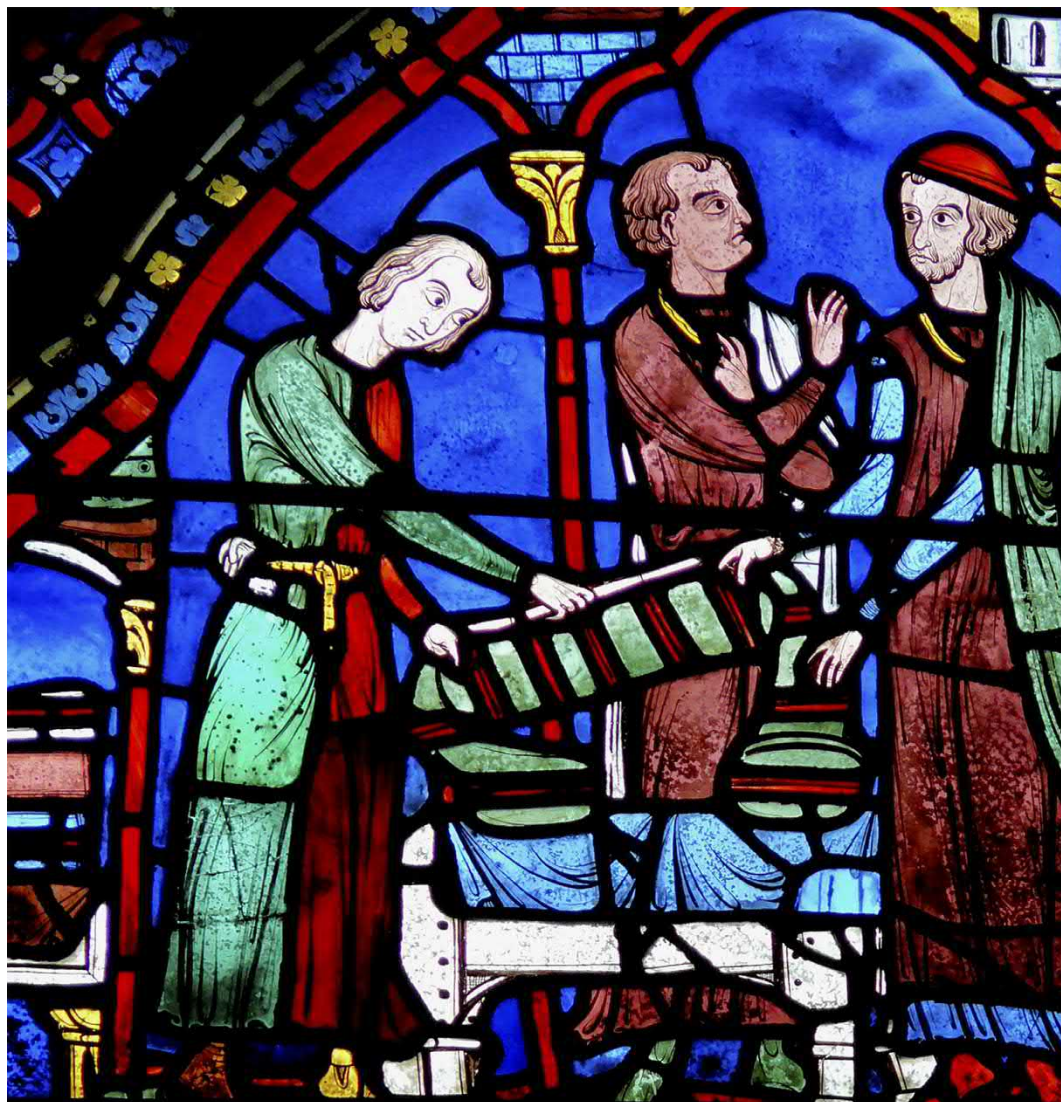


Figure 1 Coloration in a thirteenth-century stained glass of Chartres cathedral. Deep blue, tetrahedral Co^{2+} ; purple, octahedral Mn^{3+} (oxidizing conditions); light blue, octahedral Cu^{2+} (oxidizing conditions); green, mix of Cu^{2+} and Fe^{2+} (mildly oxidizing); red, ruby glass, nano Cu^0 metal (reducing conditions) (cf. Chapter 6.2). Lower right part of a window depicting the life of St. James the Greater, whose donation by the Furrier and Draper guilds is acknowledged by this scene where a client is checking fabric quality. Source: © Robert Malnoury; Martin, Inventaire général, ADAGP. (See electronic version for color figures.)

From a dual practical and scientific standpoint, no other material has been so intimately associated with light than glass because of its translucency (or transparency), of the isotropy of its optical properties, and of its limitless shapability. One can even wonder how the laws of optics and the fundamental properties of light could have been determined without glass (Chapter 10.10). Not only has this close association between glass and light not weakened in the modern world, but it has actually been strengthened to a point that could not have been guessed even in a narrow past. This section of the Encyclopedia will make it very clear.

This first chapter is a reminder of the fundamental concepts of optics provided by A. Clare who begins with light as an electromagnetic radiation to introduce the concepts of refraction, reflection, dispersion, absorption, and reemission and the manner in which these phenomena are put to use in basic optical devices (Chapter 6.1). The earliest man-made glasses were colored. It took a great many centuries before the transparency so closely associated with glass was eventually achieved. Purposely colored glass nonetheless never lost its great aesthetic appeal as so clearly illustrated by stained glass (Figure 1, Chapter 10.8). As reported by G. Calas, L. Cormier, and L. Galois, the quantum mechanical framework of solid-state physics makes it possible (i) to explain that coloration results from interactions of light with nanoparticles or with ions dissolved in well-defined sites of the glass network and (ii) to tailor rigorously light absorption for specific purposes in definite frequency ranges (Chapter 6.2).

Luminescence is another kind of light-matter interaction whereby an absorbed incident photon undergoes inelastic scattering to be reemitted at a lower frequency or, occasionally, at a higher frequency when another photon is, for example, involved. In the case of glasses discussed by L. Wondraczek, it is with rare earth and transition metal doping elements that luminescence has been optimized to give rise to special and visual effects or to technical applications such as laser gain media (Chapter 6.3). Certainly, the most important modern glass device in optics is the fiber for remote vision and especially for telecommunications without which the Internet would not exist. The challenges to make long-distance applications successful were immense, but J. Ballato shows how they have been solved at a rapid pace in terms of glass composition, purity, industrial synthesis, and drawing as well as in terms of the optical design itself and of the mono- or multimode nature of the signal transmitted (Chapter 6.4).

Without coloring elements, silicate glasses are transparent in the visible range. In contrast, they strongly

absorb light beyond 750 nm through the excitation of atomic vibrational modes. For infrared transmission, glasses with heavier and less strongly bonded atoms are thus needed to lower vibrational frequencies. The fluoride and chalcogenide systems whose structures and properties are examined by B. Bureau and J. Lucas are especially interesting in this respect as they present glass-forming compositions that lend themselves to the drawing and molding operations required to make use of their original optical properties in applications such as passive light guides or active fiber lasers and amplifiers (Chapter 6.5). Thanks to their photoluminescence, as then explained by J. Heo and K. Xu, rare earths in chalcogenide glasses are becoming significant elements in new active optoelectronic devices such as amplifiers and mid-infrared gain media either as doping ions or as *quantum dots*, i.e. nanocrystals whose optical properties become not only atomic-like (through quantum confinement effects) but tunable when their sizes reduce to a few tens of nm (Chapter 6.6).

The last chapters deal with the engineering of glass in up-to-date applications involving mainly – but not exclusively – light. Because light first interacts with the surface of a material, the variety of surface modifications reviewed by I. Sökmen, S. Oktik, and K. Bange, ranging from polishing and ion exchange to texturing and structuring, may enhance not only mechanical properties but also light transmission and absorption (Chapter 6.7). Various kinds of thin films deposited on glass surfaces are other means extensively used to modify glass surfaces. They are described by S. Oktik, I. Sökmen, and K. Bange, the best-known example being that of low-emissivity coating on window panes to improve thermal insulation (Chapter 6.8).

From the time of oil lamps, glass has been a major component of light appliances thanks to its transparency and rigidity. As reviewed by H. Yamazaki and S. Yamamoto, the changes from fire to electrical lighting in the late nineteenth century with the arc and then the incandescent, fluorescent, discharge, and xenon lamps and now LEDs and OLEDs have been made possible because each time the right glasses and forming processes have been made available (Chapter 6.9). The history of displays told by K. Maeda is similar: just as highly absorbant lead-bearing glasses had to be designed for the traditional cathode-ray tubes of TV sets, new alkali-free compositions with very high strain temperatures had to be developed to produce the now ubiquitous LCD, LED, and OLED flat-panel displays for which an outstanding mechanical stability is required at the high temperatures at which electronically active devices are deposited (Chapter 6.10).

6.1

Optical Glasses

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1 Introduction

From the first refraction measurements made in the second century (Chapter 10.10) to the current ubiquity of optical devices exemplified by communication fibers (Chapter 6.4), optics has clearly been the scientific discipline with which glass has had the tightest ties. Today, optics in fact depends so heavily on glass that specific compositions tailored for particular applications are much too numerous to be counted. In these applications, glass plays either a passive role with respect to light, changing its path, or separating different wavelengths as done by lenses or prisms, or an active role in producing light itself as in lasers and other optoelectronic devices (Chapter 6.6). The question, then, is to know why glass – predominantly oxide glass – is the archetypical material used for propagating light and interacting with light in optical devices. To answer this question in this chapter, the basics of light–matter interactions, the properties relevant to traditional optics, and the material aspects of the glass that influence them will thus be reviewed briefly. More detailed accounts are given in standard textbooks (e.g. [1, 2]) whereas a comprehensive compilation of the physical properties of glasses and other materials relevant to optics is also available [3].

Traditional optics basically relies on the laws of reflection and refraction. The former was already known in Antiquity and the latter has long been derived from Fermat's principle of least-action. According to this principle, light takes the quickest path to propagate between any two points, which is thus determined by the relative velocities at which the media are traveled as expressed by

their indices of refraction. This phenomenological approach has been extremely important to design traditional optical components and it has the advantage of being also applicable to the refraction of acoustic waves. But a much deeper understanding of optical phenomena has resulted from the discovery made by J. Clerk Maxwell (1831–1879) that light of any wavelength is an electromagnetic wave, and then from the development of quantum electrodynamics. Since then, tailoring of glass compositions for specific applications has ceased to be an empirical exercise to take instead advantage of the new fundamental physical insights gained. In preamble, it is thus useful to present a few theoretical considerations.

As an electromagnetic wave, light is made up of perpendicular electric and magnetic fields oscillating at the same frequency. It interacts with matter in ways that are controlled by the electrical and magnetic properties of the material of interest. Both are largely determined by electrical charges and the manner in which their motion and energy depend on the oscillating fields within the material. In view of their low mass, electrons are controlling many optical properties through both their number density and the relative ease with which they can move in the material to polarize it as measured by the permittivity. Depending on whether they are bound or free, electrons, for instance, cause refraction by slowing down the speed of light or undergo more complex interactions through absorption and reflection.

Be they free or bound, electrons are usually governed by band structures, which themselves strongly depend on the type of bonding within the glass and, thus, on chemical composition. Through compositional changes, this is the reason why one can vary to a large extent the electron density and the optical properties of glasses. Traditionally, however, most of these materials are electrical insulators at room temperature so that they have a wide

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bandgap and very few free electrons. Direct interaction of the oscillating electric field with electrons then is dominant. For some optical components, however, other kinds of materials are used in combination with traditional glasses to obtain a particular optical effect. If a high reflectivity is, for instance, required, metallic coatings are used because the free electrons of the metal can absorb and emit as well visible light at any frequency through their available free states. Depending upon the quality of the surface, metals can thus be very efficient reflectors of visible light.

2 Basic Features

2.1 Reflection Versus Refraction

When light hits an air–glass interface (Figure 1), it is either reflected (R) or transmitted (T_{in}) through refraction into the glass. At the second interface between glass and air, the beam T_{in} is partly reflected to be refracted again at the first interface, reinforcing R , whereas its other part (T_{out}) is transmitted and refracted into the air. Through refraction to T_{in} and inverse refraction to T_{out} , distortion is not apparent unless the glass is very thick and/or is very refractive. In the latter case, multiple reflections may occur, especially in thick glass, because reflection in an electrically insulating material depends on the refractivity difference with air, its intensity increasing with it. In short, the more refractive is the glass with respect to air, the larger the proportion of light reflected compared with that transmitted at that interface.

2.2 Angle of Incidence

A light beam traveling in vacuum consists of parallel straight lines or rays despite the fact that many sources undergo divergence. For a perfectly flat air/material interface, the *angle of incidence* is measured with respect to the normal (Figure 2). If its surface is scratched, however, then the material is hit by a light beam at many different angles so that light reflection and scattering are *diffuse*

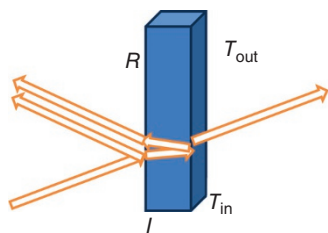


Figure 1 Reflection and refraction of a light hitting a glass surface from the left.

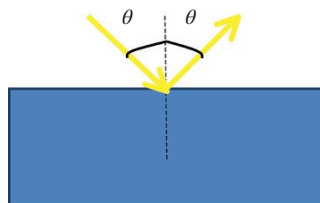


Figure 2 Light reflected by a glass surface.

because they take place at a variety of angles. A very clear *specular* reflection (from the Latin *speculum*, mirror) of an image, keeping all its details, is not possible. If the beam is reflected internally, i.e. from a glass–air interface, it may be so totally depending on its angle of incidence. It is this fundamental property that allows optical fibers to guide light (Chapter 6.4) whereas many traditional optical components rely in contrast on the fact that the extent of bending of a light traversing an interface also depends on refractive index.

In traditional optics, silicate glasses prevail because of their high transparency in the visible region. If high transparency is required, then an optically smooth surface is also needed so that one may control the light rays. And since the interfacial refractive index also controls the direction of the light beam, in traditional optics often the surface and the ultimate thickness of the component are modified so as to alter the direction of the light beam at a given position on the lateral air–glass interface.

2.3 Beam Light Characteristics

The properties of the beam light of interest must also be considered to account for the extent to which a glass causes the light to be reflected, scattered, transmitted, or altered. The wavelength distribution is a first important parameter even if one deals with only the visible region, which represents the very small fraction of the total electromagnetic spectrum where the eye has a fairly high resolution; depending on a number of factors, the lower and upper limits of this region lie at some fixed values in the ranges 380–400 and 700–780 nm. Many traditional optics experiments were originally carried out with *white* light, which is a superposition of all the visible spectral colors (Chapter 10.10). The energy, and thus frequency and wavelength, is specific to each source so that light interacts with a material in a way that strongly depends on its wavelength distribution.

White lights can have different shades depending on their color distribution and intensities. Until recently, most of those used in traditional optics were emitted by heated filament or gas-discharge lamps (Chapter 6.9). To limit spatial divergence, however, the light had to be collimated between its source and the optics. With the

invention of lasers and, more recently, of solid-state light sources, spatial divergence has been much reduced but at the price of emissions restricted to specific wavelengths. Attempts have thus been made to make white solid-state emitters but they tend to favor the shorter, and not the longer wavelength end of the visible spectrum so that their shade is blue instead of yellow as in filament sources [4].

In traditional optics, the lights of filament bulbs and discharge lamps are the least and most intense, respectively (Chapter 6.9). Much higher intensities are obtained with single-wavelength laser sources whose light is amplified and does not spatially diverge but remains collimated. Although a high intensity might seem very favorable for optical experiments, it can result in unexpected effects even at wavelengths at which the material is not absorbing because impurities or weak interactions can cause the higher intensity of electric-field oscillation to give rise to higher order, nonlinear responses to the light [5].

3 Transmitted Light T_{in}

3.1 Light Refraction

As an oscillating electromagnetic wave, light does not need a medium to propagate. When it does travel through matter, the electrons present respond more directly by a reduced wave velocity to oscillations for the electric than for the magnetic field. At a given wavelength, this slowdown is measured by the *refractive index*,

$$n = \frac{[\text{velocity of light in a vacuum}]}{[\text{velocity of light in the medium}]} \quad (1)$$

As described by Snell's law (Chapter 10.10), the difference between the angles of incidence i and of refraction r on both sides of an interface (Figure 3) thus reflects a difference between the relevant indices of refraction:

$$n = \frac{\sin i}{\sin r} \quad (2)$$

On exiting from the higher-index material on the right to the same lower-index material (Figure 3), the light is refracted away from the normal where it becomes parallel to the incident ray from the other surface.

In practice, the speed in air is often considered instead of that in vacuum. Not only was refraction generally studied at interfaces involving air but, with its index of refraction of 1.003, air is similar to vacuum in its retardation of electromagnetic radiation. In contrast, retardation is particularly important in electrically insulating solid media in which, especially at high electronic densities, bound electrons respond slowly to propagate the wave.

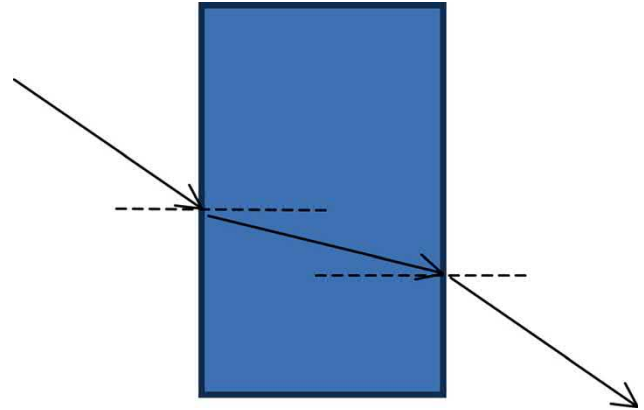


Figure 3 Light passing through interfaces where the index of refraction is changing.

3.2 Dispersion

Although lights of all wavelengths travel at the same speed in a vacuum, they do not do so in a transparent material whose response for a given wavelength depends on its number density of bound electrons. Specifically, the speed at which the electrons can respond to move the wave through the material depends on the frequency of the oscillating field (how often it increase/decreases and changes direction) and how close to one another are the electrons. Because the frequency of the field oscillation controls the velocity reduction of the wave, it causes the refractive index of the medium to depend on frequency, even in the narrow visible range and, thus, on color. This is why each color of an initially white light is refracted at a slightly different angle at an interface. This dependence of the refractive index of a medium on wavelength is known as the *dispersion* of the material. For pure silica glass, n , for instance, decreases from 1.53 to 1.4 from 0.3 to 3.6 μm wavelengths (Figure 4). If dispersion allows the different wavelengths of a light to be separated with a prism or gratings, it also results in the *chromatic aberration* that severely limits the resolution of a single magnifying lens since for a given incident beam the different wavelengths are focused at different distances (Chapter 10.10).

As a simple way to account for dispersion in the visible range, it is customary to measure the index of refraction at three well-defined wavelengths toward the end and in the middle of the visible range. The blue F-line of hydrogen at 486.13 nm (n_F), the yellow d-line of helium at 587.56 nm (n_d), and the red C-line of hydrogen at 656.28 nm (n_C) are often selected for this purpose.

When no indication is given, the reported index of refraction is n_d , which is the one referring to the middle of the visible region. The index difference between the F and C lines is the *average* or *principal* dispersion. More

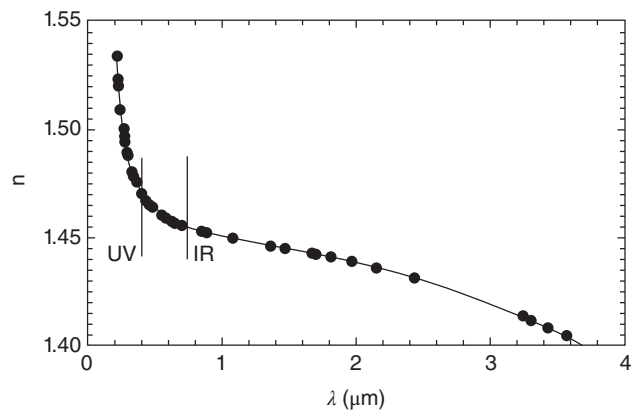


Figure 4 Index of refraction of SiO₂ glass (Corning code 7940) from the ultraviolet to the far infrared. *Source:* Input data from [6].

conveniently, the dispersion may be simply characterized by a parameter V defined by Ernst Abbe (1840–1905) in terms of the indices of refraction for red (n_r), yellow (n_y), and blue (n_b) colors, namely

$$V = (n_y - 1) / (n_b - n_r), \tag{3}$$

whose reciprocal is termed the *relative* dispersion. Along with the index of refraction, the *Abbe number* is useful for summarizing the optical properties of glasses as a function of composition (Figure 5; see also Figure 6 of Chapter 7.9). The long-standing opposition between *flint* and *crown* glasses is in particular readily rationalized in terms of V values lower and higher than 50, respectively.

An ideal optical glass would combine a high refractivity with a low dispersion. As obvious in the Abbe diagram,

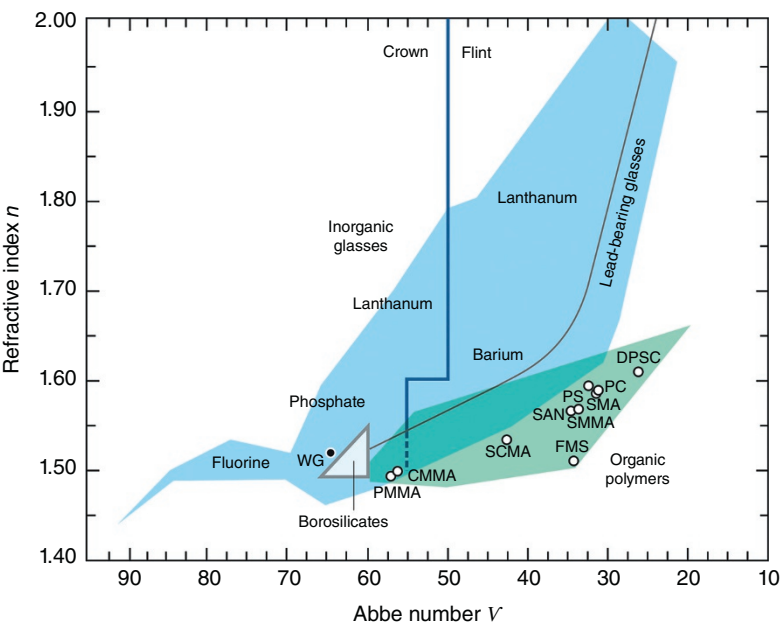


Figure 5 Abbe diagram for inorganic glasses and organic polymers. WG, soda-lime silica window glass. *Source:* After [7].

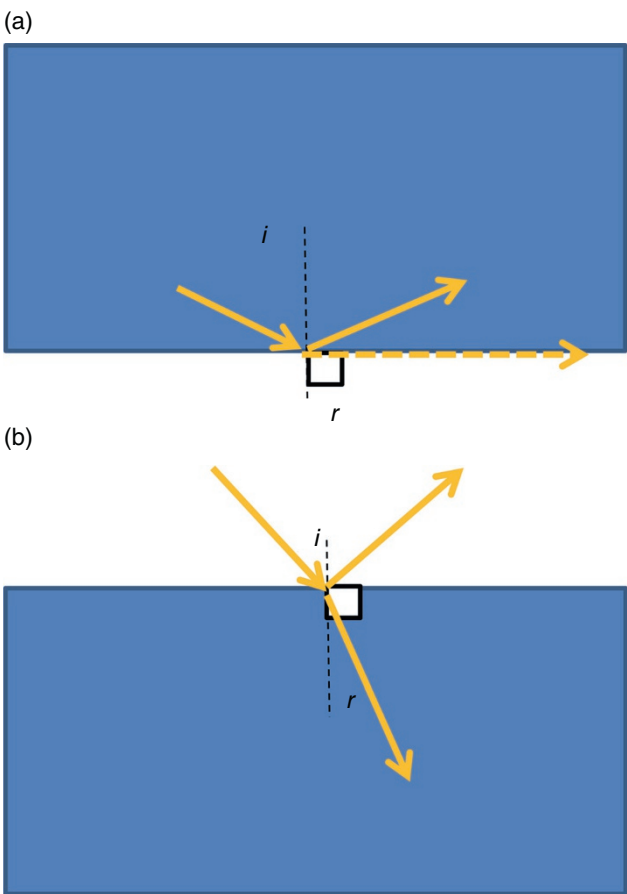


Figure 6 External refraction and total internal reflection in glass. (a) Refractive index of air to glass, $n = \sin i / \sin r$. (b) Total internally reflection at the interface between a higher- and a lower-index medium.

such a combination would actually run counter the observed trend according to which a high refractive index tends to correlate with a high dispersion. The reason is that the higher electron density that can respond to the oscillating electric field, the more the electromagnetic wave slows down whereas the electric field of the light wave is similarly slowed down by the field causing charged particles – typically the electrons – to oscillate (in the same way that a moving body is more slowed down by a denser medium). The type of material, its composition, and structure thus control the number density and types of electrons (free or bound) with which the wave interacts and, hence, the oscillations caused by the field.

For an analytical description of dispersion, one usually fits a Cauchy or Sellmeier equation to the observed wavelength–refractive index relationship. The latter equation is preferred for optical glasses [8]. If λ designates the vacuum wavelength, in micrometers, its general form is

$$n^2(\lambda) = 1 + \sum \frac{B_i \lambda^2}{\lambda^2 - C_i}, \quad (4)$$

where the summation is made over the absorption resonance peaks and the fit parameters B_i and C_i represent the

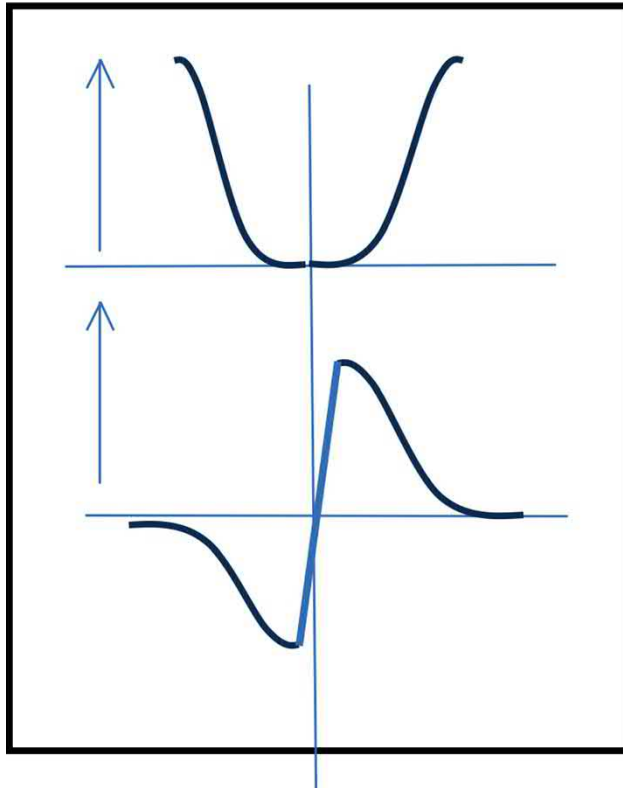


Figure 7 Relationship between absorption peak and refractive index.

strengths of these resonances and the squares of their frequencies, respectively.

Particularly in the visible range, the dispersion of optical glass becomes specially strong close to an absorption frequency where the refractive index becomes very sensitive to the wavelength because it is a function of the first derivative of the absorbance (Figure 7). This index goes through zero at the absorption peak, and then steeply increases with the wavelength until reaching a sharp maximum and decreasing. As discussed below, the origin of such a dispersion in traditional optical glasses is the ultra-violet absorption edge from electrons excited across the electronic bandgap.

3.3 Light Absorption and Re-emission

The propagation of light is also affected by absorption or scatter by the medium. The wave-particle duality requires to consider light as isolated packets of waves, known as photons, for which de Broglie relation states that

$$E = h\nu, \quad (5)$$

where h is Planck's constant and E and ν are energy and frequency. If E exactly matches the energy interval between two states of charged particles within the material (usually electrons, for visible light), then the photon may be absorbed. By inducing a change from a lower to a higher energy state in the material, the photon then finds itself eliminated from the transmitted light.

Through a sample of thickness d , the intensity I transmitted is given by Beer–Lambert law,

$$I = I_0 \exp(-\alpha d), \quad (6)$$

where I_0 is the intensity of the incident light and α the absorption coefficient at the wavelength considered. As already stated, absorption can take place if the energy of the wave oscillation exactly matches an energy interval to bring an electron from a lower to a higher level in the electronic structure of the material. If there are free electrons, like in metals, these intervals are very numerous so that many photons are absorbed and often immediately re-emitted because higher-energy states have short lifetimes. For electrically insulating materials, like traditional optical glasses, any photon whose energy exceeds an analogous interval transfers part of it to an electron so that its frequency is diminished instead in the transmitted light.

For solid materials, the energy intervals depend on the electronic structure of the individual atoms, on how these are bonded, and on the overall atomic structure of the glass. In general, the band structure of the material has to be considered. As electrical insulators, most traditional

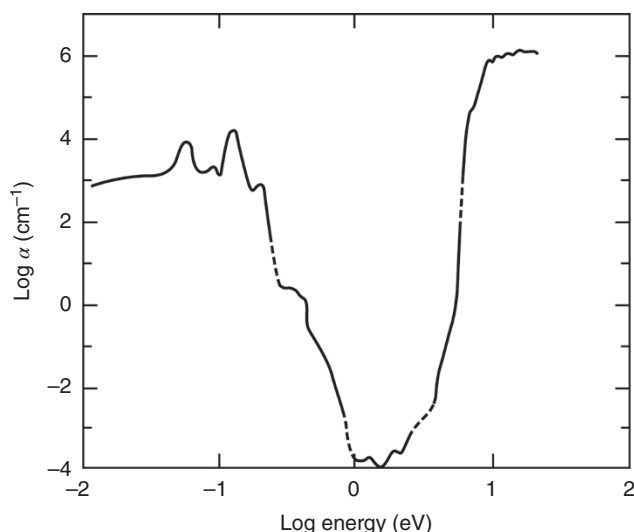


Figure 8 Absorption spectrum of window glass. Source: After [9].

optical glasses have a full valence band, a wide bandgap, and an empty conduction band. As a result, they typically absorb light only at energies higher than those of the violet end of the spectrum, which causes electrons to be excited from the valence into the conduction band over the wide gap. But many of these glasses have polar bonds, which give rise to vibrations and, thus, to absorption at infrared frequencies. By a happy coincidence, the eye is sensitive in the range where silicate glasses absorb very little between the UV and IR ranges (Figure 8). This is the very simple reason why these materials look transparent and why they have been traditionally used in optics.

But transparency may be modified, for example, by addition of colorant ions acting as filters for specific wavelengths. Typically, the absorbing ion has a low enough concentration such that it is incorporated in the network as an isolated species that keeps its distinct electronic energy levels without participating in the band structure of the glass (Chapter 6.2). As a result, color filters transmit the light that is not absorbed by the isolated ions, whose absorption coefficients vary considerably; for example, small quantities (fractions of a weight %) of cobalt oxide in glass give a deep blue color whereas similar quantities of a rare earth like neodymium oxide would give a very pale (almost invisible violet color). When promoted to higher energy levels, however, these ions tend to return to their ground state but they often do it not immediately and not directly. If the de-excitation takes place through intermediate electronic levels, i.e. at smaller energy intervals, the light emitted has a longer wavelength (lower energy). For certain ions such as some rare earths and transition metals, such a *photoluminescence* can be quite strong (Chapter 6.3).

4 Glass Properties

4.1 Bonding

In general, there are three types of primary bonding in traditional materials, namely metallic, covalent, and ionic. Most materials combine two of them, often in conjunction with secondary weaker bonding such as van der Waals.

In metals, light predominantly interacts with free electrons because, regardless of the band structure, very little energy is needed to let them oscillate. With partially filled or overlapping bands, the electronic structure of metals causes all wavelengths to be absorbed – albeit not with the same intensity – and re-emitted immediately. In traditional optics, metals have thus been used to enhance reflectivity in the form of thin polycrystalline films deposited on a glass surface. Although metallic glasses have been known for some time as ribbons or other kinds of thin samples, they are more recent in the bulk (Chapter 7.10). As a result, they have yet to make an influence in traditional optics although, if they could be made optically smooth, their enhanced corrosion resistance should be an asset to make highly reflective surfaces.

In traditional oxide optical glasses, bonding is either ionic or covalent and more typically represents a combination of the two (Chapter 2.1). The degree of covalency depends on the relative tendencies of the metallic species to give up electrons and of the nonmetal species to accept them as determined by their relative electronegativities. Two bonded species with a small or zero difference in electronegativity form a largely or completely covalent bond, respectively. If the electronegativity difference is large, the bond has an ionic character that is strong but cannot be complete.

When many atoms are present in the solid, the electron energy levels combine to form bands. In contrast to those of metallic bonds, the new atomic energy levels are usually full so that the electrons tend to be bound up in bonding. With covalent and ionic bonding, free electrons are available if the highest filled (valence) band is separated from the next highest empty (conduction) band by a gap so as to allow conduction to take place. Typically, those bandgaps are very large for solids with a predominantly ionic character. In more covalently bonded solids, they can be in contrast small enough to promote electrons to the conduction band either at room temperature or with low-energy photons.

Bonding is on average a 50 : 50 covalent ionic mix in silicate glasses, which have thus generally a large bandgap. The polarizing interactions that control the speed of light through are thus typically due to bound electrons in the material. On the short wavelength/high energy end of the spectrum, transparency is limited by the bandgap of the

material – a wider bandgap shifting transmission toward higher energies, at shorter wavelength typically in the ultraviolet spectrum. On the long wavelength end, transparency is in contrast limited by vibrational transitions of the bonds, provided their polarities make their excitation possible by the electromagnetic radiation. For most inorganic glasses, the limit to the transmission of infrared light actually depends on the strengths and masses of the bonded species, weaker bonds, and heavier bonded species allowing for longer transmission at infrared wavelengths (Chapter 6.5).

4.2 Homogeneity

Another good reason for making glass the standard transparent medium in traditional optics relates to its homogeneous, stress-free structure that can be achieved with adequate melting and annealing procedures at least at a scale larger than or equal to the wavelength of light. There is, therefore, a striking contrast with polycrystalline materials in which not only different crystallographic directions often have different light-wave velocities and refractive indices, but in which transparency is limited by reflection and refraction at grain boundaries. Wavelength-dependent processes such as Rayleigh and Mie scattering can nonetheless occur in glasses because of unavoidable structural inhomogeneity at the atomic scale. Although such processes have to be considered for optical fibers (Chapter 6.4), they do not constitute a problem for the relatively conservative path lengths of light in traditional optical components.

5 Glass Responses

5.1 Reflection

Independently of Snell's law, which rules prisms, lenses, and other optical components, changes in refractive index at an interface can also control the reflecting properties of the glass. At an interface between a low- and a high-index material, the intensity of the reflected light is greater in the latter. In a highly polarizable material, the reason is that the light is more slowed down through more interactions with oscillating electrons so that it is less transmitted and more reflected. Application of Fermat's principle to reflection then implies that the angles of incidence and reflection are the same. But whether or not one can see a reflected image depends on the aforementioned optical smoothness of the interface since roughness would result in variations of the incident and reflected angles.

In internal reflection (Figure 6), there is also an interface between the high- and low-index materials through which

refraction would take place if the angle between the transmitted light and the interface normal is larger than the angle to the same normal in the material. Since the refractive index is greater within the material than outside it, significant reflection of the light back into the glass would seem unlikely according to our previous discussion of the phenomenon. By virtue of Fermat's principle, this may nevertheless occur for a reflection angle equal to the angle of incidence to that interface. Internal reflection actually becomes significant when the angle of refraction into the low-index medium becomes 90° or higher with respect to the normal, in which case the light is wholly reflected internally. Known as total internal reflection, the phenomenon is used occasionally in traditional optics, mostly in prisms, but by far its most significant impact is its use in light transmission along optical fibers (Chapter 6.4).

5.2 Absorption

If the energy of the photons of the wave exactly equals the interval between two states of a charged particle, then the particle can transition from a low- to a high-energy state. As an obvious consequence, the number of photons of that particular energy is reduced in the light beam in a way that depends on their availability. Unless purposely doped for filtering specific visible wavelengths of light, most oxide or silicate optical glasses typically have two major fundamental absorptions to contend with that are dependent on composition. Apart from a few specialty exceptions, traditional optical glasses are not electron conductors; they have large electronic bandgaps between the upper filled valence bands and empty conduction bands. Owing to structures more disordered than those of their crystalline counterparts, glasses have less clearly defined band edges. Because of insufficient energy, however, visible light cannot enable electronic conduction through promotion of electrons across the bandgap. Only photons in the ultraviolet can do it. In this case, once the minimum energy gap is exceeded, the conduction band is wide enough to accept multiple electrons so that this energy represents more an absorption edge than an absorption peak. Hence, fewer potentially electronically conducting bonds – typically more ionic – are required for extended transparency in the ultraviolet.

At the low-energy end of the visible, it is also the oscillating electric field that interacts with the material. But in this infrared region, the energies typically couple with the vibrations of polarized bonds, which result from some ionic character associated with electronegativity differences. The frequency of the absorbed light depends upon the frequency change of bond vibrations in the glass. If bonds terminate by light elements and have a low force constant, they couple with IR radiations of lower frequencies, or longer wavelengths, which are likely transmitted

further into the infrared. Alternatively, transmission can also be achieved with a 100% covalently (nonpolar) bonded element whose vibrations do not involve polar species so that they do not couple with the electric field oscillation of the electromagnetic wave.

5.3 Glass Types for Traditional Optics

Optical glasses transparent in the visible have traditionally been made from oxides, SiO_2 being predominant. Although silica is a single-compound glass former, it tends to be used only when high purity or extended transmission into the ultraviolet is needed. The main reason is that its vitrification either requires very high melting temperatures or methods such as chemical vapor deposition (Chapter 6.4), which are both expensive. Multicomponent silicate glasses are thus usually preferred because of lower melting temperatures, easier chemical homogenization, lower viscosities, and, thus, ready casting to obtain an optically homogeneous material after careful annealing (Chapter 3.7). Specific oxides can be added to ease both melting and glass formation (typically modifiers such as alkali or alkaline earth metal oxides) and to tailor the refractive index (typically high polarizability ions such as lead), absorption (such as transition metal oxides) or photoluminescence (such as rare earth oxides) bands and other optical properties.

5.4 Engineered Glass for Specific Optical Properties

An important distinction was made in the eighteenth century between the soda-lime *crown* and the lead-bearing *flint* glasses (Chapter 10.10). Although hundreds of new compositions have been designed since the beginning of the twentieth century, this distinction remains useful to characterize the refractivity and dispersion of optical glasses, which can now be varied over large domains (Figure 5). Systematic measurements of the index of refraction made for binary metal-oxide silica systems have been especially useful in this respect (Figure 9). Replacement of SiO_2 or network-forming Al_2O_3 by heavier metal oxides, for instance, results in a higher refractivity because the polarizability is higher for nonbridging than for bridging oxygens. But that structural factors play a significant role is actually indicated by some unexpected differences or similarities. For instance, sodium and potassium silicates have the same indices, which are lower than those of lithium silicates because of structural collapse around the small Li^+ ions. As expected, in contrast, indices are higher in alkaline earth than in alkali systems, and still more so for lead silicates. From a practical standpoint, a more important feature is the almost linear

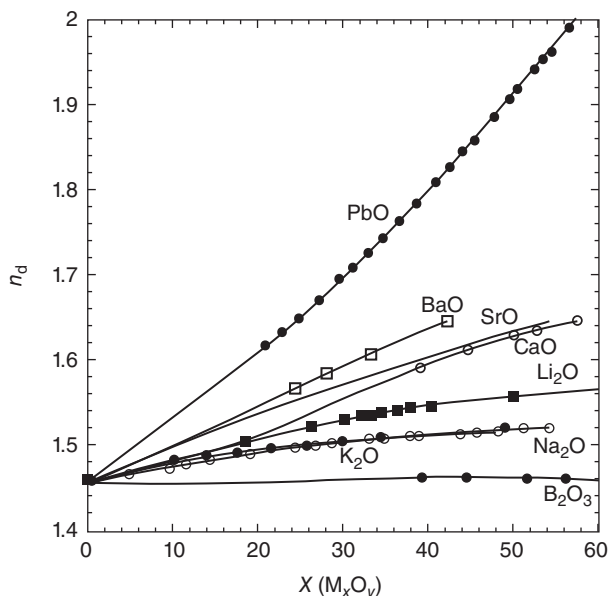


Figure 9 Effect of composition on room-temperature refractive indices at 589 nm in binary metal-oxide silicate glasses. Source: Input data from [6].

variations of n_d with composition (Figure 9). These simple trends have been the basis of empirical models of prediction of the refractive index as a function of chemical composition, which are thus extensively used as starting points in the design of new compositions.

A simple approach is based on Lorentz–Lorenz relationship between the polarizability and refractive index, which had long proven successful when applied to organic compounds. For inorganic glasses, the molar refractivity is then related to the molar volume V_m and the index of refraction at the wavelength considered by:

$$R_m = V_m (n^2 - 1) / (n^2 + 2). \quad (7)$$

And the molar refractivity of the glass is then assumed to be the sum of the ionic refractivities of its constituting oxides:

$$R_{mi} = \sum x_i R_{mi}, \quad (8)$$

where x_i is the mol fraction of oxide i and R_{mi} , for instance, varies (in cm^3) from 0.05 (B^{3+}) and 0.07 (P^{5+}) to 0.1 (Si^{4+}), 0.17 (Al^{3+}), 0.2 (Li^+), 1.33 (Ca^{2+}), 3.1 (Pb^{2+}), and 4.3 (Ba^{2+}) [10]. But a limitation of the constant values of this model is that, in turn, the molar refractivity of oxygen (O^{2-}) cannot be considered constant as it must, for instance, varies from 3.55 (in quartz) to 4.53 (in Ca_2SiO_4) or 4.97 (in Ba_2SiO_4) to agree with the experimental data [10]. More complex models of prediction of the refractive index have thus been devised (e.g. [11]), which are beyond the scope of this chapter.

Although optical glasses were traditionally transparent only in the visible, transmission in both the ultraviolet and infrared is needed for many applications (Chapter 6.5). A higher electronic bandgap is needed to increase transparency in the UV, which one achieves easily by introducing strong ionic bonds to lower the covalent character of the glass. With about 50% covalent bonding, silica itself is quite UV transmitting but its aforementioned processing difficulties offset the advantage of not needing addition of weakly bonded modifier cations. As done with chalcogenides and fluoride glasses (Chapter 6.5), the strategy for increasing the transparency in the infrared consists in decreasing the polarity of the bonds, making the bonded species heavier and weakening bonds such that the fundamental vibrational absorption edge shifts to lower energies and, therefore, to longer wavelengths.

Many optical components require a high index to reduce the volume and, thus, the weight of the glass required. Since the refractive index is raised by a higher electron density along the light ray, it would seem logical to add to the composition heavier elements with many electrons such as lead. Whereas lead was earlier used to raise the refractive index, it also makes the glass more dispersive (Chapter 10.10). In prisms, for example, this feature was an advantage but the increased optical aberration is problematic in lenses (Chapter 10.10). Other dopants such as barium and some lanthanides are thus better suited to raise the refractive index, thanks to their high electron density, because they do not significantly raise the dispersion at the same time (Chapter 10.11). The effect is probably due to the higher ionic character of the bonding of these ions with oxygen, which increases the absorption bandgap and, thus, shifts the dispersion tail to shorter wavelengths. Although it is not itself a glass former and cannot be incorporated at contents higher than 40%, La_2O_3 has proven especially effective to raise n_d up to nearly 1.73 while keeping an Abbe number lower than 1.55 [12].

6 Interaction of Optical Components with Light

6.1 Lenses

For a thin lens whose constant radii of curvature are R_1 and R_2 , the focal length (f) in air is given by the relation

$$1/f = (n - 1) (1/R_1 - 1/R_2). \quad (9)$$

In addition to the refractive index, two other factors are at play to change the propagation of light, namely the angle of incidence angle and the optical path length of the glass. Curved surfaces, for instance, mean that the

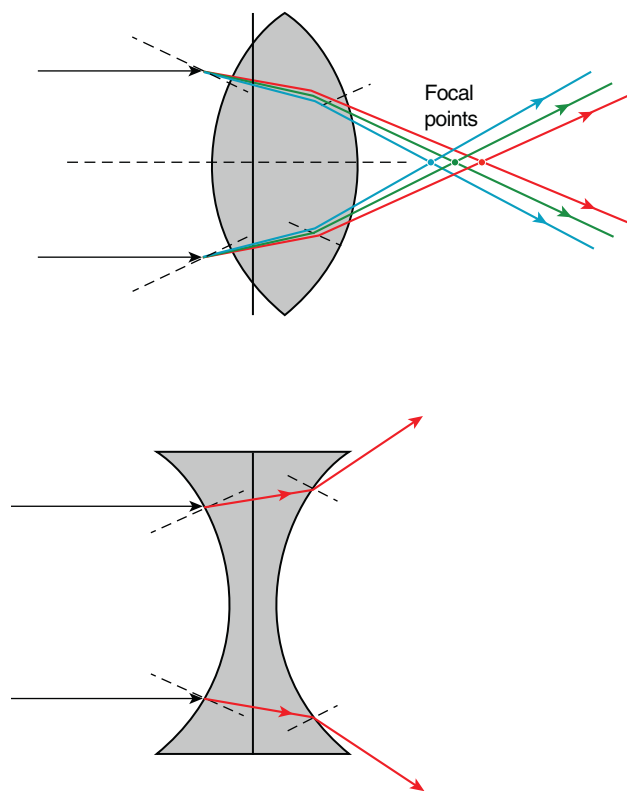


Figure 10 Refraction of a light beam coming from the left and traveling parallel to the principal axis of lenses: convergence for a convex lens, and divergence for a concave lens. Chromatic aberration resulting from focal lengths increasing with increasing wavelength from blue to red. Spherical aberration avoided if the radius of curvature of is not constant but vary such that the lens has the shape of a rotational hyperboloid.

rays from a parallel beam of light enter the glass at different angles, therefore getting refracted at different angles both in and out of the glass as illustrated by the simple convergent and divergent lenses (Figure 10). As already understood in the Middle Ages (Chapter 10.10), thanks to these two refractions, a lens constitutes a means of focusing and defocusing the rays, thus magnifying or reducing an image or changing the light to or from a parallel beam. In all cases, further control of the effects can be made through adjustments of the refractive index and/or the physical thickness profile (the two surfaces) of the glass. Originally, the lenses used for early optical experiments were made from *crown* or *flint* glasses which were polished and ground to acquire a shape that would allow the rays of the light to be redirected as needed in the particular application. More modern optical glasses use barium as a compositional additive to raise the refractive index as it reduces the hazards associated with manufacturing components. In principle, with more modern techniques for fabrication such as chemical vapor deposition (cf. Chapter 6.4), it is even possible to produce a

functional gradient in the refractive index of a parallelepipedic piece of glass to achieve the same lens effects.

6.2 Mirrors

Like analogous lenses, a convergent mirror focuses the light whereas a divergent mirror spreads it. The fraction of light reflected is given by the reflectivity (R), which depends on the indices of refraction of the two media involved, on the angle of incidence, and on light polarization. For normal incidence, polarization is not relevant and the reflectivity reduces to

$$R = |(n_1 - n_2)/(n_1 + n_2)|^2. \quad (10)$$

For a crown glass ($n = 1.5$) in air, the reflectivity thus is 4%.

As reflective optical components, mirrors are made by application of a thin layer of metal to a pristine glass surface. Many mirrors for optical experiments and instrumentation require the metallic film to be deposited on a shaped substrate such as spherical, or even parabolic, again to allow control over the direction of the light rays. Glass was typically used because it is easy to mold and subsequently machine/polish to a desired shape. For a low precision (e.g. decorative) mirror, the metal can be applied to the rear of the glass so as to be protected from mechanical damage. But the accuracy of the image reflected by the metal layer can be impacted by the optical transmission within the glass plate. For high-precision optics, therefore, the metal is applied to the atomically flat front surface of the glass. The glass substrate for the metallic surface can be molded, machined, and polished to be anything from plane to spherical or parabolic surface depending on the intended function of the mirror. The metal used for optics in the visible region was originally a tin/mercury amalgam before the much less hazardous silver could be deposited in the nineteenth century. Today, a good reflectivity is achieved with either silver or aluminum to which a little copper is added. With modern techniques, a large variety of coatings are in fact commonly deposited in several layers to ensure good bonding and protection against oxidation (Chapter 8). For infrared light, gold may be used as the reflective metal.

6.3 Filters

Filtering out a single or a range of wavelengths to ensure that only specific frequencies are allowed to pass usually requires the band structure of the glass to have dopant quantities of colorant species (Chapter 6.2). Many of these ions are either transition metals or rare earths. There are some limited glasses with other dopants such

as uranium or other actinides. In the early days of optical filters, transition metal ions were used because for many of them the d-block absorptions gave an intense color in the visible for only a modest dopant level. The main problem with these outer d-block orbitals is that the ions can have different oxidation states, whose energies are impacted by the surrounding anions, their number, their geometry, and their bond length. Known as the ligand-field effect, this feature is the principal reason why a particular transition metal such as chromium can produce different colors in different oxide environments (Chapter 6.2).

6.4 Prisms and Gratings

Highly refractive glasses were often used for prism to disperse white light into its individual colors. Thanks to their higher dispersion, the original flint glasses were thus preferred in these applications. In more modern experiments, diffraction gratings are often favored because they can be work both in reflection or in transmission. In a grating, slits or grooves with a spacing d wider than the wavelength of the light of interest act as individual point sources interfering with one another constructively or destructively depending on the incident angle:

$$d \sin \theta_{\max} = m\lambda. \quad (11)$$

The order m of the diffraction strongly depends on the shape of the grooves. In view of the difficulties met when machining them on the original glass substrates, however, grooves are now generally ruled on polymer substrates with holographic rather than mechanical techniques.

7 Perspectives

From optical benches in research laboratories to modern telescopes, microscopes, and cameras, inorganic glasses have no competitors for high-quality optics owing to an unmatched capability to tailor their refractive and dispersive properties in wide domains through compositional adjustments (Figure 5). The prospects for widening further these domains are weak, however, because the effects of all economically affordable elements have already been investigated. Actually, some of them like thorium, beryllium, or cadmium would be of interest but their use is ruled out for obvious environmental reasons. In parallel, the quality of the glass itself has been much improved. Some of the defects that plagued early opticians remain present, but at extremely low levels. Improvements in melting procedures and batch homogenization combined with a better understanding of relaxation processes (Chapter 3.5) makes it, for instance, possible to achieve

indices of refraction constant to within $5 \cdot 10^{-7}$ and to reduce bubbles to levels so low that their total cross sections can be only 0.006 cm^2 in a volume of 100 cm^3 [12]. At the same time, mechanical and physical properties and chemical resistance to the atmosphere, stain, acids, alkalis, or phosphates have also been optimized for the intended conditions of use.

A review of only the most important current applications of optical glasses is clearly beyond the scope of this chapter. Homogeneous glass is the basic component of the tens of lenses, mirrors, and beam splitters assembled on optical benches to propagate or condition light, in particular for a wide variety of spectroscopy experiments (Chapter 2.2) that can be made on samples as small as a few microns directly observed under extreme conditions of temperature or pressure. Likewise, the simple design of the original microscopes and telescopes has been replaced with very complex setups (e.g. [13, 14]). In a modern microscope, a single objective may, for instance, consist of a set of up to 15 lenses to correct all kinds of aberrations, reduce background noise, and yield sharp images even at large fields of view. For obvious reasons, thinner and more lightweight lenses are preferred, which implies higher refractive indices.

In the design of such instruments, computer modeling has largely taken over traditional optical-table experiments to determine the shape and type of glass needed for a particular component and to test and verify their intended combinations. But inorganic glasses can be very good at producing some unexpected results at the physical modeling stages of the making the components so that some compositional iteration may still be required at this stage.

Concerning the resources, one should note that traditional inorganic glasses requires much energy to be synthesized but also that the raw materials used are quite plentiful and relatively inexpensive. We might thus see a resurgence of inorganic glasses for traditional optical applications, especially where large volumes are required, as a way toward a greener environment.

In at least two important applications, inorganic glasses have nonetheless been replaced by organic polymers (Chapter 8.8) whose lightness, resistance to mechanical shock, and easy forming have been major assets. These are eyeglasses and lenses for cell phones, tablet computers, or personal assistants with market sizes of the order of billions of units in each instance. The quality achieved in the latter case by lenses with a focal length of 4.5 mm yielding a resolution ranging from 0.3 to 12 MP is a real technological feat, especially when one considers that these lenses are produced by injection molding at a very low price – from 3 to 5 US\$ in the early 2010s – and that a mechanical zoom is not common for cost and size

reasons [7]. As impressive as they are, polymers nonetheless suffer from intrinsic limitations. These are clearly revealed by a comparison of their Abbe diagram with that of oxide glasses (Figure 5), which points to a rather narrow range of refractive indices so that inorganic glass thus remains without rival for high-precision optics. As for their lesser sensitivity to temperature and the improvements currently made in terms of scratch resistance, they are important practical advantages that give them another edge over polymers.

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6.2

The Color of Glass

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1 Introduction

Color has been a most attractive feature of glass for millennia, from the glazes and pearls of the Suse period (4000 BCE) to the elaborated Roman houseware at the beginning of our era and to the stained glasses that blossomed during the European Middle-Ages. The kaleidoscope represented by medieval stained glasses (Figures VI and 1) illustrates the wide range of coloration of these glasses. The analysis of the coloration mechanisms gives information on the elaboration conditions, redox, and fining conditions.

The control of color throughout the synthesis process is a key component of glassmaking. This importance was underlined by Weyl's founding book, "*Colored glasses*," where much of the knowledge on this topic available in the 1950s was summarized [1]. In present-day technology, functional glasses are often developed because absorption bands within UV and IR regions give rise to specific applications. This is, for instance, the case of iron-bearing glasses for which the main absorption band of Fe^{2+} in the 1000–1200 nm region makes efficient absorption of solar energy possible, while keeping light transmission in the visible range sufficient to ensure adequate visibility through car windshields. On a more general basis, the limited energy range in which oxide glasses are absorbing, because of the presence of (un)wanted impurities, does not preclude these glasses to be commonly transparent in the near-IR (Chapter 6.1), which is an important parameter for modeling the diffusive radiative transport.

The color of a glass depends on light absorption, scattering, or reflection at wavelengths in the

immediate vicinity of the visible spectral region. As other coloration processes, it depends also on the incident light source used and on the observer's eye sensitivity. In the absence of coloring agents such as chemical impurities, defects, clusters, and nanophases, most oxide glasses are colorless because they do not absorb visible light. This is the very reason for their extensive use as components for optical instruments or communications, e.g. silica glass for light transmission down to 160 nm, beyond the transmission domain of the Earth's atmosphere.

In the presence of impurities or structural defects, glasses are colored by selective absorption in specific regions of the visible spectrum. Optical absorption then gives indications on the nature and structural environment of coloring species and, in turn, on glassmaking parameters such as batch composition, furnace atmosphere, melting temperature, or duration of the melting process. Glass color is an exemplary illustration of structure–property relationships in glasses [2] through the connection between the atomic-scale structure of the glass and the nature and the intensity of the absorption bands that cause glass coloration. As will now be shown, the physical mechanisms behind coloration can be ligand-field effects, charge-transfer processes, or quantum-confinement effects in metal or semiconductor nanoparticles.

2 Background on Color Processes

2.1 Light Transmission by Glasses

The color of glass arises from variations in the light transmission efficiency throughout the visible spectrum, which lies between about 400 and 800 nm (Chapter 6.1). At the origin of coloration are absorption bands or

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absorption edges whose effects are measured in terms of light transmission T through a glass plate

$$T = I/I_0, \quad (1)$$

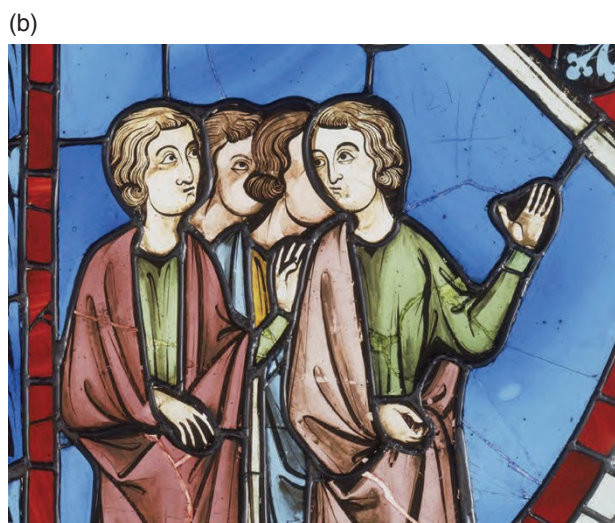


Figure 1 French stained glass from the thirteenth century (cf. Figure VI). (a) Notre-Dame of Chartres cathedral (1215–1240), Bay 5, James and Josuas, detail of The life of St. James the Greater (cf. Figure VI), Chartres. © Malnoury, Robert; Martin, J., Inventaire général, ADAGP. (b) Sainte Chapelle, Paris (1245–1250). © RMN (Musée de Cluny, Paris). (See electronic version for color figures)

where I_0 and I represent the intensities of the incident and transmitted light, respectively. Reflection losses occur at glass–air interfaces, however, but they are readily accounted for because the intensity of the incident (I_{in}) and reflected ($I_{\text{Reflected}}$) beams are related by

$$I_{\text{Reflected}} = I_{\text{in}} (n - 1)^2 / (n + 1)^2, \quad (2)$$

where n is the index of refraction of the glass. For a soda-lime-silica glass ($n = 1.523$), Eq. (2) indicates that a fraction f of approximately 0.04 of the incident beam is reflected at each interface, regardless of the wavelength in the visible region where n varies by about 0.01.

Because light absorption depends on both glass thickness (l) and concentration of coloring elements (c), a more fruitful assessment of the process relies on Beer–Lambert law, which relates for a given wavenumber the absorbance A to these parameters and to the molar absorption coefficient ϵ (also known as molar extinction coefficient, or molar absorptivity)

$$A = \log (I_0/I) = \log (1/T) = \epsilon cl. \quad (3)$$

The ratio A/l is referred to as the linear absorbance, allowing comparison between samples with different thicknesses. As indicated by Eq. (3), the transmission as a function of wavelength and absorbance as a function of wavenumber are easily interconverted. For a soda-lime glass, however, the two representations do not carry the same information in the visible and near-infrared spectral regions (Figure 2). Whereas transmission is the property of interest in practical applications, the absorption spectrum has to be considered instead in order to understand the coloration mechanisms because its bands can be assigned to definite structural components. Transmission to absorbance interconversion is probably one among the most spectacular structure–property relationships in materials.

At short wavelengths (or high wavenumbers), one observes the onset of UV absorption, which is due to electronic transitions between the valence and conduction band tails across the bandgap. This absorption edge can be described by another absorption coefficient, α , which follows an exponential Urbach-type law as a function of the wavenumber ν ,

$$\alpha \sim \exp (h\nu/E_u), \quad (4)$$

where E_u is the Urbach energy that accounts for the energy distribution of the localized states in the valence band tail. On this absorption edge are superimposed intense charge-transfer bands, also located in the near UV, which have a Gaussian lineshape (see Section 5).

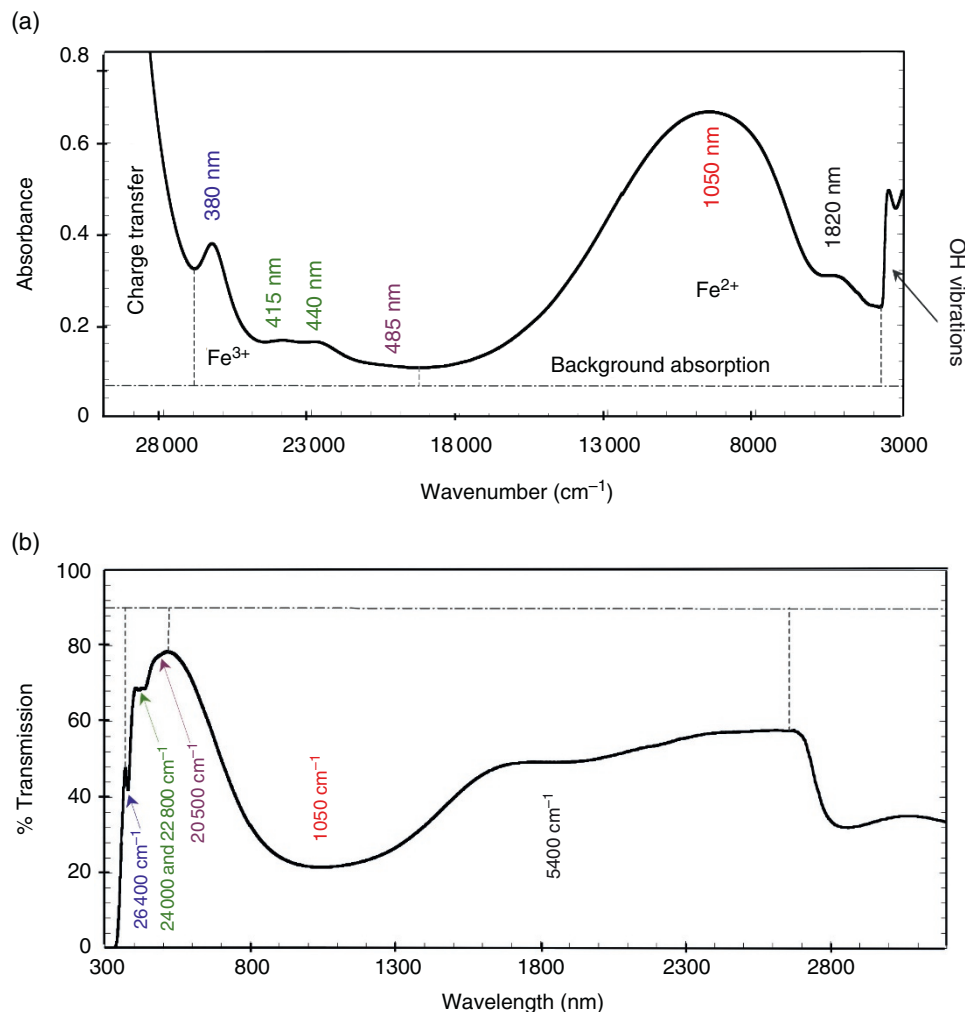


Figure 2 Glass coloration as examined from the standpoints of absorption and transmission for a soda-lime silicate glass containing 0.87 wt % Fe_2O_3 (sample thickness 4 mm). In the absorbance spectrum (a), the electronic transitions of Fe^{2+} and Fe^{3+} are clearly apparent in the near IR and visible-near UV, respectively. As to the transmission spectrum (b), it is used to represent coloration and provides colorimetric parameters. *Source:* After [3]. (See electronic version for color figures)

2.2 The Role of Transition Elements as Coloring Agents

The color of glass is generally due to electronic transitions in transition elements between localized electronic energy levels that are split by the ligand field. Transition elements are characterized by the presence of unpaired electrons in partially filled d- or f-orbitals. Electronic transitions within these orbitals are at the origin of selective light absorption at characteristic energies, usually within or in the vicinity of the visible spectrum [4]. The energy and intensity of these transitions vary as a function of the transition metal ion present, its oxidation state, and its immediate surrounding (site symmetry, nature of the ligands).

As d–d transitions are parity forbidden according to the selection rules for electric dipole transitions (Laporte

rule), transition elements in principle should not have a high coloring efficiency. This feature holds particularly true for 4f-elements, in which the electronic levels retain an atomic character because 4f-orbitals are shielded by the outer electronic shells and not admixed with other electronic states. Hence, the molar absorption coefficient of lanthanides is 5–10 times smaller than that of 3d elements, yielding only faint colors even at concentration levels of several wt %.

For d-transition elements, the d-orbitals are not shielded by outer orbitals so that there is some admixture with other states when there is no inversion center at the site occupied by the transition element (distorted sites, tetrahedral or 5-coordinated sites). This admixing partially relaxes the Laporte selection rules, making 3d-elements such as Fe, Cu, Cr, V, Mn, Co, and Ni the major

coloring agents in glasses. Two main mechanisms are involved: (i) electronic transitions between crystal-field split 3d-electronic levels; (ii) charge-transfer processes, i.e. a transfer of the electronic density between the transition element ion and its ligands or other neighboring transition elements. As compared with the former, the latter is allowed and then results in an intense coloration. In both cases, optical transitions depend on the speciation of the transition element, namely its oxidation state, coordination number, site distortion, and on the nature of the chemical bond with its ligands (Table 1).

2.3 The Sites Occupied by Transition Elements in Glasses: A Limited Disorder

The fact that glass coloration can be assigned to one or several species of transition elements indicates the presence of well-defined cation sites. It is thus an obvious inadequacy of the Zachariasen model of oxide glasses not to describe the local environment of cations. During the last decades, many experimental studies and numerical simulations have demonstrated that the structure of oxide glasses and melts is more organized than assumed with a continuous random network. They have shown that cations are not restricted to fill holes within the polymeric network but tend to define their own environment according to the well-known crystal-chemical rules that exist in crystals. A major advance has thus been this conclusion that cations have a heterogeneous structural distribution, which contributes to an original medium-range order of oxide glasses and makes it possible to explain charge-transfer processes involving transition elements.

Because of a usually lower density caused by atomic disorder, the coordination number of cations is generally lower in glasses than in crystals of similar composition. Some cations mimic network formers by occurring in tetrahedra connected to the polymeric network within a well-defined topology: such are the cases of tetrahedral Ni^{2+} , Zn^{2+} , and Fe^{3+} . Network modifiers are cations such as alkalis or alkaline earths that are 6- or higher-coordinated. Contrary to what is observed in crystals, however, few transition metal ions are octahedrally coordinated in glasses and there is no evidence for higher coordination of 3d ions. The most important ions adopting an octahedral coordination are trivalent and highly charged cations such as Cr^{3+} , V^{3+} , or Zr^{4+} , as well as Co^{2+} and Ni^{2+} in the special case of alkali-poor borate glasses where they occur as CoO- and NiO-derived 2-D-nanodomains.

Other transition metal ions such as Fe^{2+} , Ni^{2+} , and Fe^{3+} are frequently distributed among various site geometries whose proportions and resulting effects on color depend on chemical composition. They are often 5-coordinated – a coordination seldom observed in crystals – which gives rise to original colorations. This structural evidence points to the presence of small sites where cations have a structural role intermediate between those of network formers and modifiers. But the fact that transition metal ions cause well-defined optical absorption spectra in glasses indicates that their site distribution is limited despite the amorphous structure of these materials. The need for satisfying the charge neutrality of ligands implies a connection to the glassy polymeric network and indicates that a concept of quasi-molecular complexes does not describe the actual structural location of these ions.

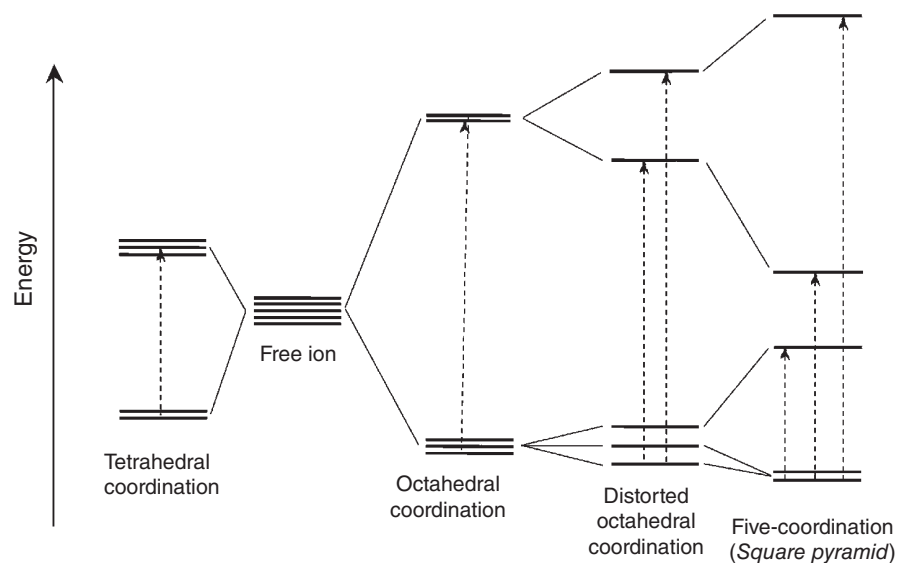


Figure 3 Successive splittings of d-orbitals of transition elements in different coordination numbers and site geometry. The dashed lines represent the electronic transitions that can be observed in a one-electron system.

3 Crystal-Field-Driven Glass Color

3.1 Crystal-Field Effects

The relative energy of d-orbitals varies as a function of the coordination number and distortion of the site occupied by the transition element, and by the bond covalency with the ligands. All these factors give rise to characteristic splittings (Figure 3) that make transitions between these electronic levels possible with a selective absorption of light that causes glass coloration. The position of these electronic levels gives indications on the local symmetry and magnitude of the ligand field splitting.

The intensity of these transitions is determined by selection rules for which the spin state of the transition

metal ions plays an important role since absorption bands are less intense when the transition implies a change of the electron spin. For instance, Mn^{2+} and Fe^{3+} are not efficient coloring agents because both ions have five electrons occupying the five d-orbitals (Figure 4a), which leaves room for only spin-forbidden transitions of low intensity. Although less abundant than Fe^{3+} in glasses melted in air, Fe^{2+} gives them their characteristic green coloration caused by the presence of an intense absorption band in the near-infrared because a sixth 3d-electron (Figure 4a) produces spin-allowed electronic transitions. This contrast is reflected in the molar absorption coefficient of these ions, which is an order of magnitude lower for Fe^{3+} relative to Fe^{2+} (Figure 4b). Molar extinction

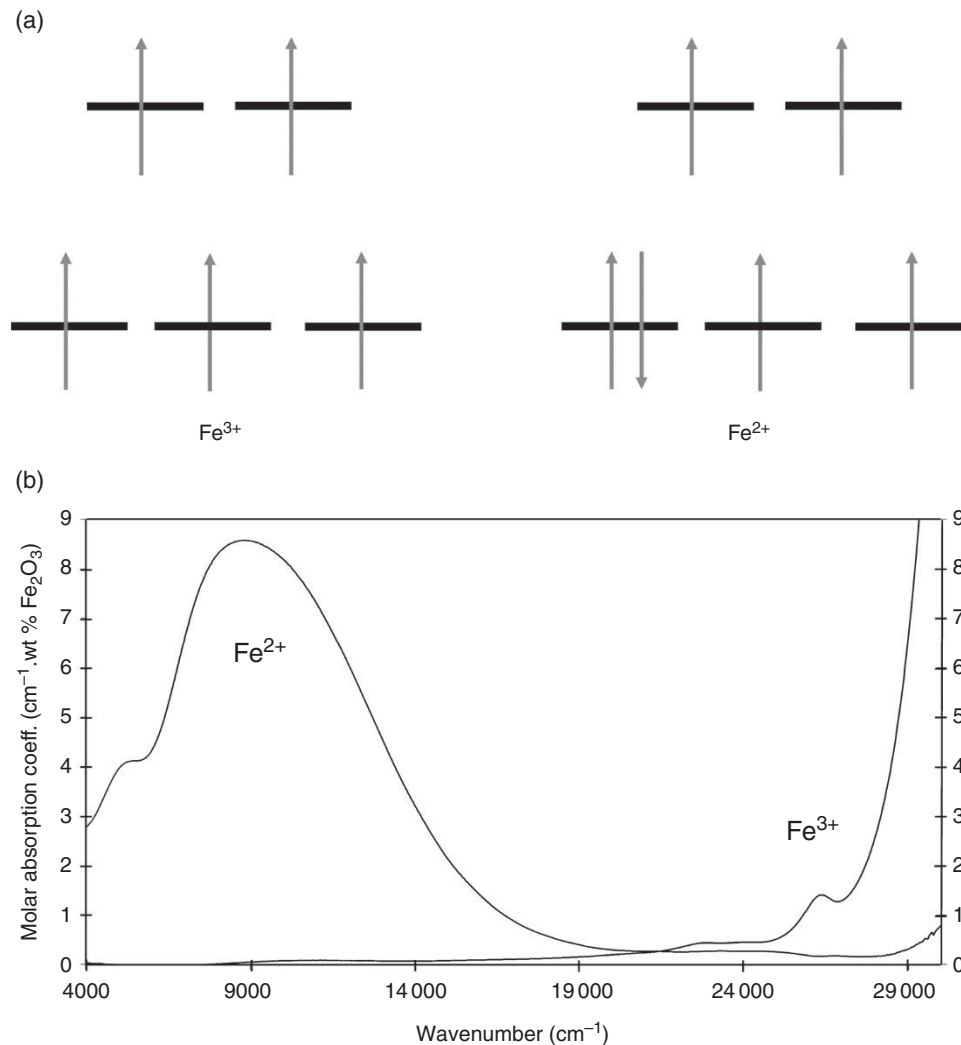


Figure 4 Influence of the electronic configuration on the optical absorption efficiency of Fe^{2+} and Fe^{3+} . (a) Schematic representation of the population of 3d orbitals. For Fe^{3+} , five electrons occupy the five d-orbitals so that d–d transitions are forbidden. For Fe^{2+} , the sixth electron gives rise to an electronic transition. (b) Spectral dependence of the molar absorption coefficient of Fe^{3+} and Fe^{2+} in a soda-lime-silica glass. Source: After [3]. The large difference in coloring power between these oxidation states results from the different electronic configuration shown in (a).

coefficients are important to model optical absorption spectra in glasses, provided the chemical composition of the glasses be similar: as optical properties are additive, it is possible to compute optical absorption spectrum expected from the presence of various coloring elements (Table 2).

Finally, another factor to be taken into account is the electrostatic repulsion between 3d-electrons because it influences the optical absorption spectra by shifting the free-ion electron energy levels prior to the action of crystal field. This interelectronic repulsion can be expressed in terms of three parameters A, B, and C known as the Racah parameters (after Giulio Racah, who first described them). Racah parameters are ion-specific and for a given ion vary with the electron localization (i.e. with cation-ligand bond covalency). The reduction of interelectronic repulsion between the 3d-electrons corresponds to a more covalent character of the transition metal ion oxygen bond.

3.2 Peculiar Sites, Peculiar Colors: The Example of Ni^{2+}

Nickel yields colors ranging from brown and yellow in Na-, Li-, or Ca-bearing glasses to purple or blue in K-,

Rb-, or Cs-bearing glasses or, less commonly, green or even orange in some alkali-deficient borate and borosilicate glasses (Figure 5). This broad palette of hues in oxide glasses is directly related to the varying coordination of Ni^{2+} [6]. Probably one of the most commonly observed colors, the brown arises from continuously decreasing absorption from the purple to the red parts of the visible domain along with the absence of an absorption maximum in the visible domain. That color is indeed very sensitive to local structure as shown by a comparison between the optical absorption spectra of crystalline and glassy $\text{CaO} \cdot \text{NiO} \cdot 2\text{SiO}_2$ (Figure 6). The former has the light green color characteristic of $^{[6]}\text{Ni}^{2+}$. In the latter, Ni^{2+} occupies a small proportion of tetrahedral sites but it is mostly present in triangular bipyramids that give rise to the brown color through a broad, asymmetric absorption band around $22\,500\text{ cm}^{-1}$ (444 nm). Weak and broad absorption bands in the visible and near-infrared correspond to the other electric transitions expected for $^{[5]}\text{Ni}$. The existence of these $^{[5]}\text{Ni}$ sites has been confirmed by complementary Ni K-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopy and neutron diffraction coupled with isotopic substitution. As underlined below for Fe^{2+} , however, most methods do not

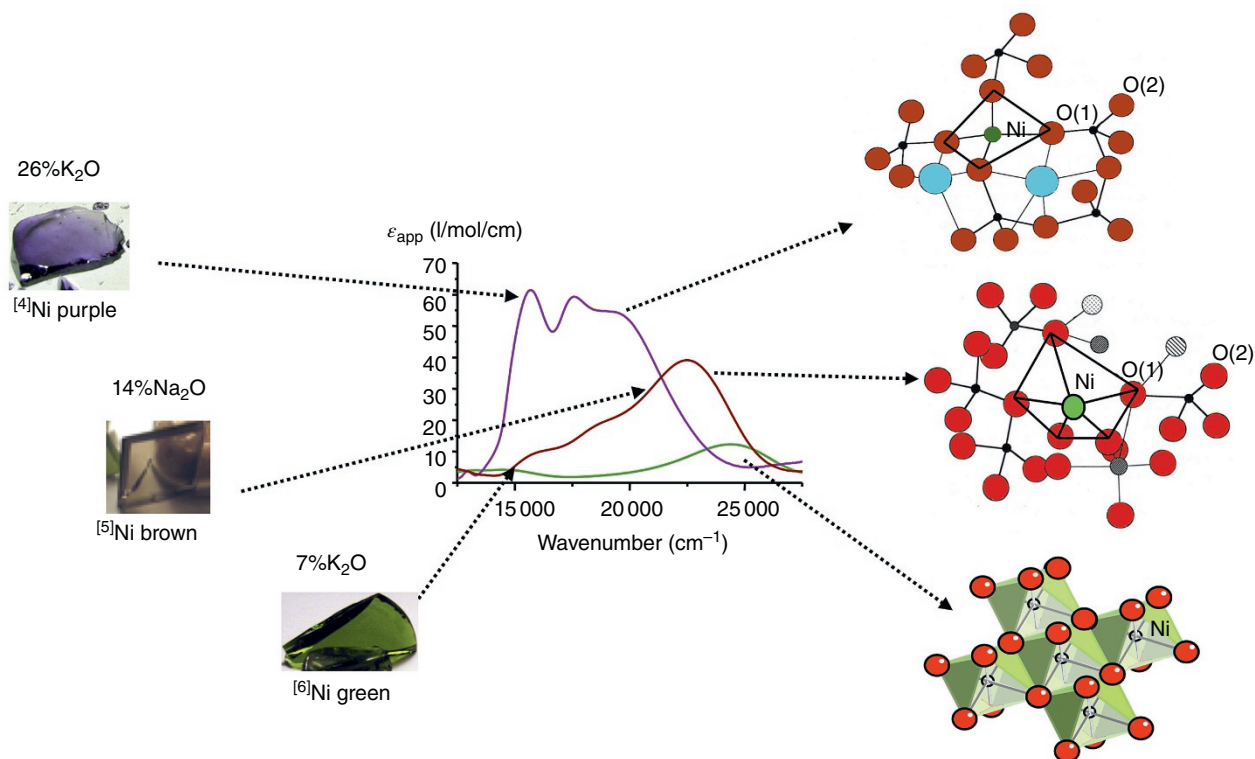


Figure 5 Optical spectra and structural models explaining the color of purple, brown, and green borosilicate glasses containing Ni^{2+} in four-, five-, and sixfold coordination, respectively. Source: After [5]. (See electronic version for color figures.)

provide indication on the actual site geometry of the ^{55}Ni site, which has been mostly derived from optical absorption spectroscopy.

Optical transitions from tetrahedral Ni^{2+} are present as a minority contribution in most optical absorption spectra of Ni-bearing silicate, aluminosilicate, and borosilicate glasses, with the noticeable exception of low-alkali borate or borosilicate compositions. In glasses containing large alkalis (K, Rb, Cs), $^{44}\text{Ni}^{2+}$ causes a blue/purple coloration through the presence of an intense absorption band located near $16\,000\text{ cm}^{-1}$, in the red region of the visible spectrum, and a transmission window at short wavelengths (Figure 5). This chemical dependence of glass coloration will be discussed in Sections 4.1 and 6.1.

3.3 Peculiar Sites with a Continuous Site

Distribution: Fe^{2+} and Fe^{3+}

Although iron is the most common coloring element in glasses, the geometry of the sites occupied by Fe^{2+} and Fe^{3+} is still a matter of debate in spite of numerous studies made with a broad range of structural and spectroscopic methods that includes X-ray and neutron diffraction, Mössbauer spectroscopy, electron paramagnetic resonance, XANES and EXAFS, optical absorption, and luminescence (Tables 1 and 2).

Like for Ni^{2+} , there is no evidence for octahedral coordination of Fe^{2+} in silicate glasses, but the picture is less clear-cut for Fe^{3+} . The optical absorption spectrum

of Fe^{2+} shows two absorption bands, the most intense near 9000 cm^{-1} with an extension to higher wavenumbers in the red region that also affects glass coloration. A significant absorption down to $16\,000\text{ cm}^{-1}$, i.e. outside the absorption domain of octahedral Fe^{2+} in crystals, indicates the presence of ^{55}Fe . A detailed magnetic circular dichroism study has confirmed that the Fe^{2+} absorption band is mostly caused by four- and fivefold coordinated species [7]. This result agrees with Mössbauer and Fe K-edge XANES and EXAFS data, which indicate that Fe^{2+} coordination varies continuously from four- to

Table 1 Glass coloring mechanisms.

Cause of coloration	Examples	Efficient concentration
Crystal-field transitions	d-Elements	0.1–10 wt % ^a
Atomic-like transitions	4f-Elements	1–10 wt %
Ligand to metal charge transfer	O– Fe^{3+} , O– Ce^{4+} , S^{2-} – Fe^{3+} , O^{2-} –U(VI)	10–1000 ppm
Intervalence charge transfer	Fe^{2+} – Fe^{3+} , Fe^{2+} – Ti^{4+}	1–10 wt %
Nanoparticles	Au^0 , AgCl, Cd(S, Se)	10–100 ppm

^a Lower efficient concentrations for $^{44}\text{Co}^{2+}$ (some 10–100 ppm) and 4d- and 5d-elements (e.g. Pt^{4+} : a few 100 ppm).

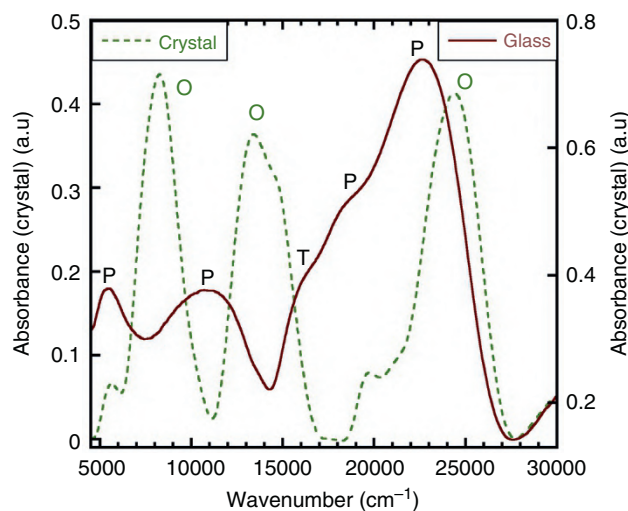


Figure 6 Effect of nickel coordination on the absorbance spectra (derived from diffuse reflectance) of $\text{CaNiSi}_2\text{O}_6$ crystal and glass which are green and brown, respectively. The position of the three similarly intense peaks of octahedral Ni^{2+} in the crystal (O) contrast with the two weak peaks and the large high-energy band produced by Ni^{2+} in the trigonal bipyramids of the glass (P), to which tetrahedral Ni^{2+} contributes a shoulder (T). Source: After [6]. (See electronic version for color figures.)

Table 2 Color yielded by various transition metal ions in glasses.

Oxidation state	Coordination number	Color
Ti^{3+}	6 (distorted)	Lilac
V^{4+} (VO^{2+})	6 (distorted)	Blue
V^{3+}	6	Green
Cr^{VI} (CrO_4^{2-})	4	Yellow
Cr^{4+}	4	Blue
Cr^{3+}	6	Green
Cr^{2+}	6 (distorted)	Blue
Mn^{3+}	6 (distorted)	Purple
Mn^{2+}	4, 5	Light yellow/orange
Fe^{3+}	4, 5	Light yellow
Fe^{2+}	4, 5 (6?)	Green
Co^{2+}	4	Violet blue
Ni^{2+}	6	Apple green, yellow
Ni^{2+}	5	Brown
Ni^{2+}	4	Blue, purple
Cu^{2+}	6 (distorted)	Blue
Pt^{4+}	6	Yellow

fivefold. These complementary techniques do not provide further information on the actual site geometry of ^{55}Fe sites, however, which may range from a square pyramid to a trigonal bipyramid geometry. Optical absorption spectra are very sensitive to this variation in the local symmetry that gives rise to distinct electronic transitions. A modification of the geometry of the ^{55}Fe site as a function of glass composition may explain the variations observed in the position of the broad Fe^{2+} absorption band near $10\,000\text{ cm}^{-1}$ in glasses. This continuous distribution thus contrasts with the bimodal distribution between discrete site geometries observed for Ni^{2+} , each one being characterized by well-defined spectroscopic parameters.

Owing to experimental difficulties, the interpretation of the Fe^{3+} optical absorption bands in glasses has also been much discussed. It nonetheless appears that (i) the most intense bands arise from field-independent transitions that do not depend on site geometry; (ii) the other crystal-field transitions are superimposed on and can be obscured by the tail of the intense O–Fe charge-transfer transitions that occur in the near UV; (iii) as underlined in Section 3.1, Fe^{3+} transitions are spin-forbidden and hence of lower intensities than those of Fe^{2+} by more than one order of magnitude. In a recent investigation of glasses in which iron was fully oxidized, however, Fe^{3+} speciation could be unambiguously determined by EXAFS [8]. Providing information on the origin of the transitions observed in the optical absorption spectra, this study clearly showed that Fe^{3+} coordination is changing from 4 to 6 as a function of the nature and concentration of the alkali and alkaline earth cations present, the coordination number of Fe^{3+} increasing with decreasing cation ionic radius ratio. Alkali–alkaline earth glasses show evidence of a stabilization of $^{44}\text{Fe}^{3+}$, illustrating a preferential link between ^{44}Fe and the alkalis [8] and indicating that transition metal ions are not probing the average glass structure, but favor some local surroundings.

3.4 Presence of One Site Geometry: Cr^{3+}

Like in most crystalline compounds, Cr^{3+} occurs in glasses only in octahedral coordination because of the high crystal-field stabilization energy of the d^3 configuration. The crystal-field spectrum of Cr^{3+} exhibits two broad, intense bands at $15\,000$ and $22\,000\text{ cm}^{-1}$, which occur in the visible range and have characteristic Gaussian line shapes with bandwidths close to that observed in crystals (Figure 7). This is consistent with the observed Cr–O interatomic distances and their small radial disorder determined by Cr K-edge EXAFS. These absorption bands define transmission windows near $10\,000$, $18\,000$, and $27\,000\text{ cm}^{-1}$: only the second one is responsible for the characteristic green color observed in Cr-bearing

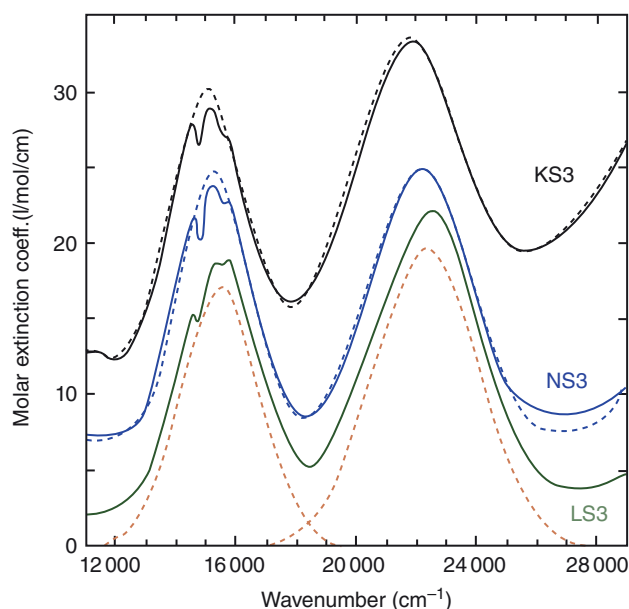


Figure 7 Molar extinction coefficients of Cr^{3+} in K-, Na-, and Li-trisilicate glasses (referred to as KS3, NS3, and LS3, respectively); experimental spectra (solid curves) and fits made with Gaussian bands (dashed curves), which are also plotted as dotted curves for LS3. For clarity, the data for NS3 and KS3 have been shifted upward by 2.7 and 12 l/mol/cm, respectively. Source: After [9] (See electronic version for color figures.).

glasses since the others are outside the visible spectrum. Additional weak features near the maximum of the bands are linked to field-independent spin-forbidden transitions, resulting in characteristic interference dips.

Other transition-element cations exhibiting only one site geometry in glasses include Ti^{3+} , V^{3+} and V(IV) (actually the vanadyl group, VO^{2+}), Cr^{2+} and Cr^{4+} , etc. Special mention must be made of Mn^{3+} and Cu^{2+} for which the main absorptions band undergo Jahn–Teller splitting of the excited e_g level through spontaneous distortion of the octahedral coordination, which increases the crystal-field stabilization energy. As a result, Mn^{3+} allows light transmission in the red and violet part of the visible spectrum, resulting in the characteristic pink/magenta color of Mn-bearing glasses, whereas Cu^{2+} exhibits a unique, large transmission window in the blue-green part of the spectrum.

3.5 The Case of Silent Species: Co^{2+} -Bearing Glasses

The typical blue color of Co-bearing glasses is due to an intense absorption band located in the orange and red parts of the visible spectrum that is characteristic of $^{44}\text{Co}^{2+}$ (Figure 8). This assignment from optical absorption spectroscopy is in agreement with XANES and EXAFS data. Even though the hue of Co-bearing glasses

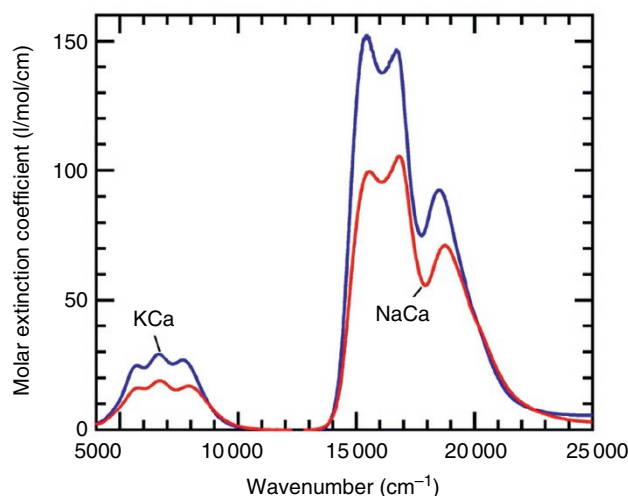


Figure 8 Influence of the nature of the alkali cation on the intensity but not on the lineshape of the optical absorption bands of Co^{2+} -bearing $\text{K}_2\text{O}\cdot\text{CaO}\cdot 4\text{SiO}_2$ (blue) and $\text{Na}_2\text{O}\cdot\text{CaO}\cdot 4\text{SiO}_2$ (red) glasses. Absorbance is represented as represented by the molar extinction coefficients, allowing quantitative comparison between the two glasses. Source: After [10]. (See electronic version for color figures.)

does not vary much with glass composition, the intensity of the coloration (and hence of the absorption bands) does change. As an example, replacement of K by Na in $\text{R}_2\text{O}\cdot\text{CaO}\cdot 4\text{SiO}_2$ ($\text{R} = \text{K}, \text{Na}$) glasses decreases the optical transition intensity by 35% whereas the molar extension coefficient of $^{[4]}\text{Co}^{2+}$ complexes is only half of the values reported for potassium and sodium silicate glasses. This is an indication that Co^{2+} converts to less absorbing, *silent* species when replacing a given alkali by either a smaller alkali or alkaline earths. As indicated by EXAFS data, the smaller molar extension coefficient cannot be attributed to a distortion of the Co tetrahedral site, as observed in crystals. These observations suggest the presence of higher coordinated, weakly absorbing species, that are difficult to quantify because the optical absorption bands of $^{[4]}\text{Co}^{2+}$ overlap the transitions expected for $^{[5]}\text{Co}^{2+}$ and $^{[6]}\text{Co}^{2+}$. Although the low intensity of these spectroscopically silent species does not help in recognizing them in optical absorption spectra, they directly affect the intensity of light absorption and hence the efficiency of Co^{2+} as a coloring agent.

4 Variation of Glass Coloration

4.1 Dependence of Color on Glass Composition

Changing glass composition affects the effective charge of the oxygen ligands, and hence crystal-field splitting magnitude as well as cation-oxygen covalence. Transition elements are indeed interesting structural probes of glass

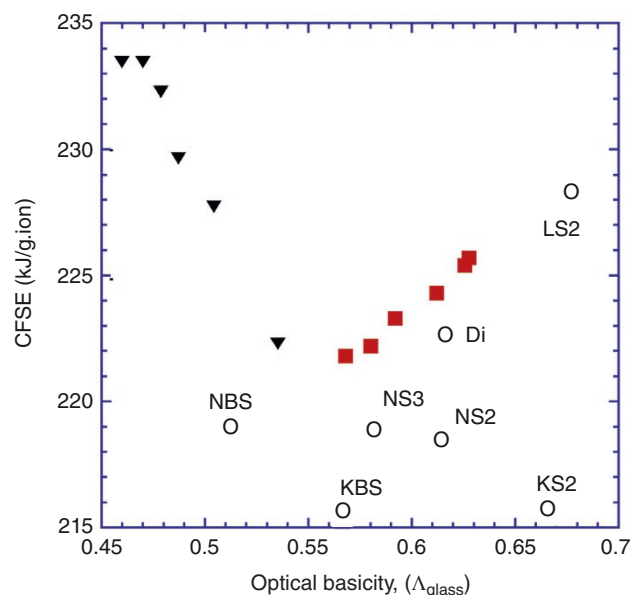


Figure 9 Variation of Cr^{3+} crystal-field splitting, represented as the crystal field stabilization energy (CFSE), as a function of optical basicity in glasses. Filled squares: multicomponent silicate and aluminosilicate glasses, which mimic chemical variations during magmatic differentiation; open circles: alkali silicate glasses (NS, KS, and LS refer to sodic, potassic, and lithic silicate glasses, respectively, NBS and KBS stand for sodium and potassium borosilicate glasses) and Di for diopside ($\text{CaMgSi}_2\text{O}_6$) glass; filled triangles: alkali borate glasses. Source: After [11].

structure. Two different cases can be distinguished in this respect. When only one site geometry exists (e.g. Ti^{3+} , Mn^{3+} , Cr^{3+} , V^{4+} , and V^{3+}), the chemical dependence of the optical spectra manifests itself mostly through a shift of the main absorption bands. When two sites (e.g. Ni^{2+} , Ti^{4+}) or more (e.g. $^{[4]}\text{Fe}^{2+}$ and $^{[5]}\text{Fe}^{2+}$, $^{[8]}\text{Nd}^{3+}$ and $^{[9]}\text{Nd}^{3+}$) are present, their relative proportions vary with glass composition without much shifting of the electronic transitions. An abundant bibliography exists in this domain, but is mostly restricted to some specific glass systems. We will illustrate this section with Cr^{3+} and Ni^{2+} .

4.2 Variation of Site Geometry: Presence of a Single Type of Site

The case of Cr^{3+} has been studied extensively. This cation retains a regular octahedral coordination in most oxide glasses [11] in spite of some variations in the magnitude of crystal-field splitting and of disorder effects induced by glass composition mostly as a function of the nature of the modifier cation (but not of its concentration). In multicomponent glasses (Figure 9), the crystal-field intensity increases with optical basicity (cf. Chapter 5.7). In alkali silicate glasses, however, it varies only with the nature of the alkali and not with its concentration. In mixed

alkali-alkaline earth glasses, optical absorption parameters in addition remain close to the values found in binary silicate glasses with the same type of alkalis, which reveals that Cr^{3+} shows a strong preference for alkalis in its immediate environment. These observations indicate that Cr^{3+} is insensitive to the overall glass structure. It builds instead its own environment, which is also demonstrated by its heterogeneous distribution in the glass structure [11].

4.3 Variation of Site Geometry: Presence of Two Sites

When a glass bears an ion such as nickel that distributes between two sites, its color varies with glass composition [6] as the fractions of $^{[5]}\text{Ni}^{2+}$ and $^{[4]}\text{Ni}^{2+}$ sites. In silicate glasses, alkalis and alkaline earths are either network modifiers when they coexist with $^{[5]}\text{Ni}$ or charge-compensators for $^{[4]}\text{Ni}$. The mean Ni speciation thus depends only on the nature of the alkali or alkaline earth. As observed in Section 4.2 for 3d-ions in a single type of site, however, the concentration of the alkali or alkaline earth does not influence glass color in silicate glasses. By contrast, in borate and borosilicate glasses, the Ni-site geometry and color progressively change with increasing alkali or alkaline earth content from octahedral (green) to distorted octahedral (yellow), trigonal bipyramid (brown), and finally tetrahedral (purple). This trend likely arises from the interaction of alkali and alkaline earths with boron when its coordination changes from $^{[3]}\text{B}$ to $^{[4]}\text{B}$ with increasing alkali/alkaline earth concentration. As a consequence, some borosilicate glasses show a peculiar orange color that is otherwise rarely encountered. In this case, Ni has the three coordination numbers 6, 5, and 4: $^{[6]}\text{Ni}$ is probably associated with the borate sublattice, and $^{[5]}\text{Ni}$ and $^{[4]}\text{Ni}$ with the silicate sublattice.

4.4 Redox Equilibria and Glass Coloration

The influence of the redox state on glass color has been much investigated [12]. For instance, Cr-bearing glasses show a change in glass color from green to yellow when melting conditions vary from reducing to oxidizing. This trend is due to the formation of a chromate complex $(\text{CrO}_4)^{2-}$ that gives rise to a charge-transfer transition from oxygen to chromium located near $28\,000\text{ cm}^{-1}$ in oxidized glasses (Figure 10). The tail of this intense band extends from the UV to the visible and is superimposed on the Cr^{3+} absorption bands because there exists a considerable difference between the molar extinction coefficients of Cr^{3+} and Cr^{6+} , which are 18–20 and $4200\text{ l}/(\text{cm}/\text{mol})$, respectively. As a result, optical spectroscopy measurements of the chromium redox state cannot be made

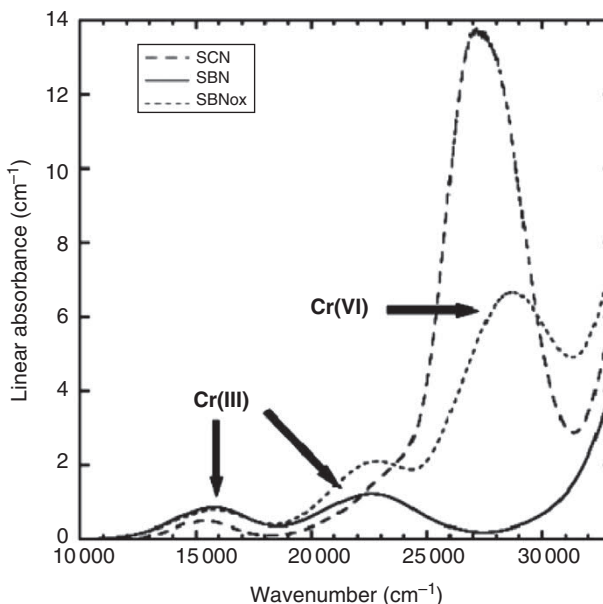
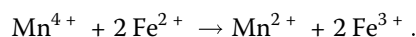


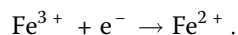
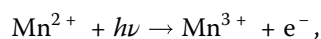
Figure 10 Linear absorbance spectra of Cr^{3+} and $(\text{CrO}_4)^{2-}$ in soda-lime-silica (SCN) and sodium borosilicate (SBN and SBNox) glasses. The position of the absorption bands characteristic of the two oxidation states of chromium in the glasses is indicated. *Source:* After [14].

on glasses in the presence of relatively high concentrations of Cr^{6+} in the form of chromate groups. Wet chemical analysis or other spectroscopic methods have to be performed instead.

The interaction between redox pairs is widely used during glass fining. For instance, manganese has traditionally been known as the *glassmaker's soap* because, if added to soda-lime-silica glass in the form of an oxide such as MnO_2 , it makes the green color arising from iron impurities less intense by oxidizing Fe^{2+} into Fe^{3+}



And because only spin-forbidden transitions are associated with the d^5 configuration of both Mn^{2+} and Fe^{3+} (Figure 4a), their low intensities result in weakly colored glasses. The effect is not permanent, however, as the interaction with sunlight (solarization) favors the reverse reactions:



As illustrated by old windows and doorknobs, this phenomenon is at the origin of the well-known *purple glass* of which *desert amethyst glass* is a natural variety.

5 Temperature Dependence of the Optical Absorption Spectra of Glasses: Thermochromism

Color changes are often spectacular upon heating: brown Ni-bearing glasses, for instance, turn blue or green Cr³⁺-bearing glasses into yellow (Figure 11). Like for the chemical dependence of glass coloration, there is a marked difference between transition elements depending on whether they occupy one or several sites. In the latter situation, temperature modifies the equilibrium between the site populations whereas in the former, the site of the coloring element expands with increasing temperature. Because of the difficulty of recording high-temperature optical absorption spectra, however, data are scarce so that we will restrict ourselves to discussing investigations made below T_g . We nonetheless warn that important modifications of the optical spectra may take place in the molten state.

5.1 Coexistence of Well-Defined Sites: Ni²⁺

In a classic piece of work, Lin and Angell [15] investigated the optical absorption spectra of Ni²⁺ in a potassium triborate glass and melt to 1000 °C. In the starting glass, Ni²⁺ is distributed between 4- and 5-coordination as in most oxide glasses (see Section 3.1). Major changes occur in the vicinity of T_g , above which the proportion of ^[4]Ni²⁺ increases. This is likely related to

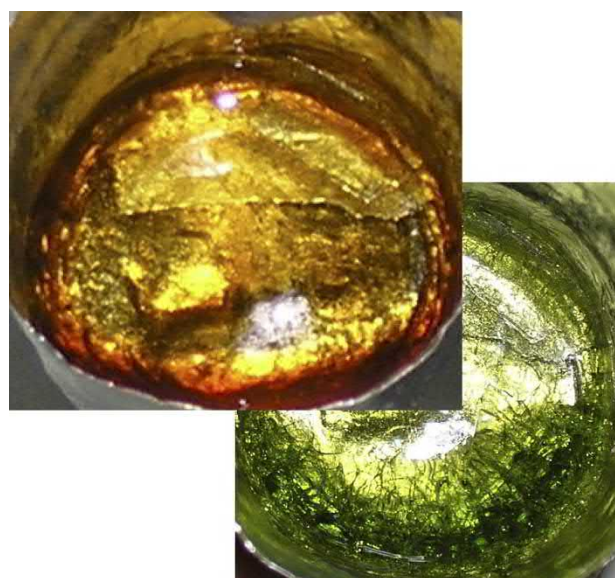


Figure 11 Green Cr-containing glasses turning yellow at ca. 500 °C, a direct illustration of the thermal expansion of cation sites in glasses. (See electronic version for color figures)

the temperature-induced coordination changes of boron, as shown by the reaction



where Na_{CC} and Na_{NM} stand for charge-compensating and network-modifying Na, respectively, and O_{NBO} for non-bridging oxygen. The ^[4]B to ^[3]B conversion between glass and melt increases alkali activity and then provides further charge compensation for ^[4]Ni, inducing the coordination change of Ni. In the borate composition investigated, the ^[4]Ni/^[5]Ni ratio is not frozen in at T_g , as these two states are separated by unusually small energy barriers. The presence of further changes down to room temperature is a direct evidence of ionic mobility while the polymeric network is frozen in. The modification of Ni- and Co-speciation in glasses at high temperature may be retained after fast quenching. This has been recently shown in Co- and Ni-bearing alkali borosilicate glasses in which the 4-coordinated species, favored at high temperature, are partly retained at room temperature by a fast quenching, illustrating the importance of thermal history on glass structure [16].

5.2 Presence of One Site: Direct Evidence of a Thermal Expansion of Cation Sites

The crystal-field strength is a sensitive probe of the environment of transition elements in crystalline compounds and of its changes under high temperatures or pressures. High-temperature optical spectra of Cr³⁺ in glasses show a systematic linear redshift of the crystal-field transition from 300 to 800 K, with an isobestic point near 17 000 cm⁻¹ (Figure 12). The transmission window similarly

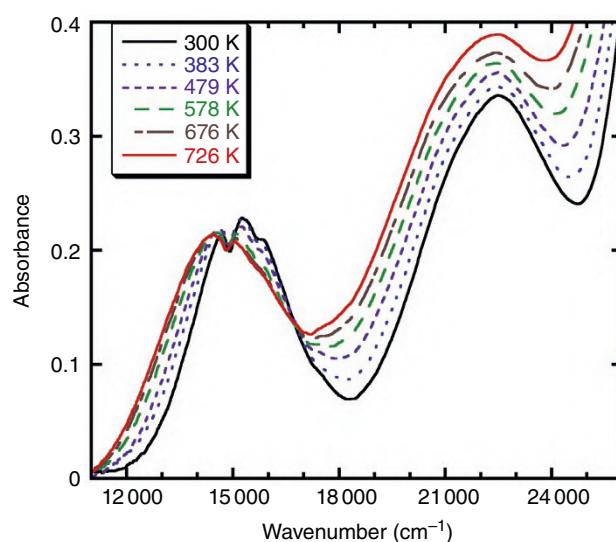


Figure 12 Modification of the optical absorption spectrum of Cr³⁺ in a potassium borosilicate glass from 300 to 726 K. Source: After [12]. (See electronic version for color figures)

shifts toward lower wavenumbers, giving glasses thermochromic properties [11]. Using a point charge model, one may derive the temperature-induced variation of the Cr–O distances from crystal-field splitting, Dq

$$10Dq = \frac{5q\langle r^4 \rangle}{\bar{R}^5} \quad (6)$$

where q is the effective charge in the ligands, r the d-electron-core distance, and $\bar{R}$ the mean Cr–O distance. In this way, one estimates the linear thermal expansion coefficients of Cr³⁺–O bonds in glasses to be about $16\text{--}20 \cdot 10^{-6} \text{ K}^{-1}$. These values are independent on glass composition, contrary to what is observed for bulk thermal expansion, and they are in addition generally larger than the macroscopic thermal expansion coefficients. This lack of sensitivity of Cr³⁺ to the average glass structure is an additional confirmation of the heterogeneous structure of silicate glasses at the atomic scale [11]: Cr³⁺ does not explore an average glass structure but rather adjusts its own environment.

6 Charge-Transfer Processes: From Amber Glasses to Lunar Glasses

6.1 Ligand to Metal Charge Transfer (LMCT)

Charge transfer (CT) represents a shift of the electron charge density from one ion to a neighboring one. The most frequent processes involve transition metal ions such as Fe²⁺, Fe³⁺, Ti⁴⁺, Ce³⁺, Ce⁴⁺, and their ligands (O, S, Se...) in relation with the covalency of the chemical bond. They give rise to intense absorption bands at short wavelengths, providing a strong UV absorption in glasses that would otherwise be mostly transparent in the visible range. These glasses are thus used for solar protection and they also ensure efficient UV absorption in food containers.

The reduction of glass transparency in the UV arises from the presence of Gaussian-shaped absorption bands, superimposed on an exponential Urbach absorption edge and related to the presence of ligand-to-metal CT transitions. The intensity of these bands is larger by about three orders of magnitude than that of crystal-field transitions. The O^{2–}–Fe³⁺ CT band near $45\,000 \text{ cm}^{-1}$ dominates the shape of the UV absorption edge [17], and may be detected at low concentration down to ppm levels. For Fe²⁺, CT is about three times less intense and occurs at slightly higher energy than for Fe³⁺. Likewise, Ce³⁺ and Ce⁴⁺ are strong UV absorbers in glasses where, as observed for iron, absorption is more efficient (by a factor of 16) and takes place at higher wavenumbers for the oxidized than for the reduced form [18]. Other transition

metal ions show intense ligand-to-metal transitions in the UV, e.g. near $33\,000 \text{ cm}^{-1}$ for Ti⁴⁺ [19].

Increasing the covalency of Fe–ligand bond shifts the energy of the charge-transfer transition toward lower values. Such is the case of the well-known amber chromophore, which is widely used to efficiently absorb UV radiation and then protect radiation-sensitive liquids in glass containers (pharmaceuticals and beverages). This chromophore shows optical transition near $23\,500 \text{ cm}^{-1}$ with a molar extinction coefficient of about 9000 L/mol/cm (as compared to 25 L/mol/cm for the Fe²⁺ absorption band near 1000 nm). As a consequence, the amber chromophore contributes to glass coloration at concentrations as low as a few ppm: the high intensity of these bands causes them to extend into the visible spectrum. The continuously decreasing absorption from the violet to red gives rise to this characteristic brown coloration. The structure of this amber chromophore is still poorly known, involving ^[4]Fe³⁺ ions surrounded by one S^{2–} and three O^{2–} ions. Its stability field is then limited by two opposite redox reactions, i.e. the reduction of ferric iron and the oxidation of sulfide ligands.

A peculiar case concerns oxyanion and oxycation complexes such as chromate (CrO₄)^{2–}, vanadate (VO₄)^{3–}, or uranyl (UO₂)²⁺ groups. Under oxidizing conditions, these complexes are similar in glasses to those observed in crystals and aqueous solutions, retaining similar spectral properties. As a d⁰ system, the formal Cr(VI) or V(V) oxidation states do not have d electrons, so that the only electronic transitions occur via charge-transfer processes from ligands to the central ion, which is at the origin of the intense coloration arising from these extreme oxidation states. For instance, CT in chromate groups consists of a transfer of an oxygen p electron, constituting one of the ligand bonds of t₁π symmetry, to the central ion d-shell. Further splitting by crystal field gives rise to two absorption bands near $37\,000$ and $27\,000 \text{ cm}^{-1}$ [20]. Only the latter is usually observed because the former is hidden by the absorption of the matrix (Figure 12).

6.2 Intervalence Charge Transfer

Another type of CT involves cations with different oxidation states, which also relies on an extended covalency of chemical bonds and give rise to absorption bands so intense that these may even result in efficient coloration at concentrations down to the ppm level. Increasing the iron content in oxide glasses, for instance, increases absorption in the visible region between ligand-to-metal CT in the near UV and crystal-field transitions in the near IR so that high-Fe glasses melted in air are black (Figure 13). Evidence has been found for a contribution near $14\,500 \text{ cm}^{-1}$, assigned to Fe²⁺–O^{2–}–Fe³⁺ intervalence charge transfer (IVCT), Fe²⁺ and Fe³⁺ playing the

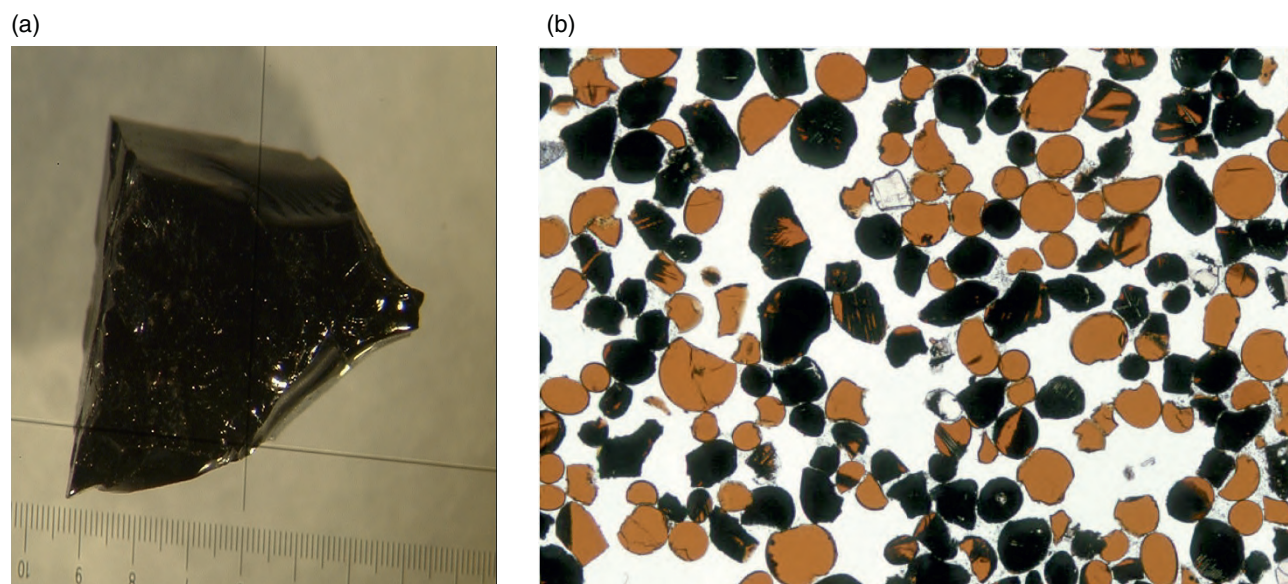


Figure 13 Coloration arising from charge transfer processes. (a) Dark color of $\text{NaFeSi}_2\text{O}_6$ glass (Fe^{2+} – Fe^{3+} intervalence charge transfer). (b) Orange glass (“soil”) collected during the Apollo 17 mission. Clear orange beads owe their color to Fe^{2+} – Ti^{4+} intervalence charge transfer. The black color of some grains comes from the surface nucleation of olivine crystals with intergrown ilmenite (FeTiO_3) crystals. Source: © Kurt Hollocher, Geology Dept, Union College, NY. (See electronic version for color figures)

role of electron donor and acceptor, respectively [21]. The deep-brown to black color of these glasses is an interesting visual proof for clustering of transition element in glasses with a significant covalent bonding in and between the Fe sites.

During lunar exploration, an original 3.48-billion-year-old orange glass has been found near a small crater at the Apollo 17 landing site (Figure 13). This glass color comes from a Fe^{2+} (donor)– O^{2-} – Ti^{4+} (acceptor) charge-transfer transition near $24\,000\text{ cm}^{-1}$. Synthetic glasses containing Fe or Ti and synthesized under simulated reducing lunar conditions exhibit a green or a purple color, respectively. It is only the association between the two transition elements that results in this original color [19]. This fact provides further proof of the heterogeneous distribution of transition element cations in glass structure, favoring a location in specific enriched regions. Similar Fe–Ti IVCT may be used for enhancing UV absorption in container glasses for drugs and cosmetics.

7 Absorption by Organized Clusters and Nanophases

7.1 Presence of Organized Clusters: Low-Alkali Borate and Borosilicate Glasses

Nickel- and cobalt-bearing alkali-poor borate glasses exhibit original green and light pinkish purple colorations, respectively. Similar colors are found in borosilicate

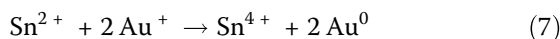
[6] but not in silicate glasses. For decades, these features have been assigned to the presence of Ni and Co in octahedral sites within the glass structure. More recently, Ni- and Co–K edge EXAFS data on these glasses have revealed cation–cation correlations up to 6 Å in ordered NiO- or CoO-based clusters and characterized by three colinear, edge-sharing octahedra, which induce a specific multiple scattering feature around 6 Å . Some structural features characteristic of the bulk oxides (CoO or NiO) are missing, however, showing that these ordered domains do not correspond to pure oxide crystallites [2]. This environment is not affected by Ni or Co concentration and disappears with increasing alkali content.

The presence of similarly ordered domains in low-alkali borosilicate glasses shows that ^{61}Ni (and probably ^{61}Co) is preferentially associated with a borate rather than with a silicate sublattice. This local coordination is likely favored by the geometrical constraints induced by the presence of rigid large ^{11}B -based superunits. But the EXAFS data indicate a less extended structural order in the NiO nanodomains, probably due to the mutual interaction between borate and silicate sublattices, which limits their extent [6].

7.2 Metallic Nanoparticles

Although *Ruby* glasses have been known for centuries (e.g. the famous fourth-century Lycurgus cup), their deep ruby-red or yellow colors have been explained only

recently in terms of precipitation of Au, Cu, or Ag nanoparticles 5–100 nm in diameter [22]. These nanoparticles form during thermal treatments above the annealing temperature of colorless starting glasses prepared under reducing conditions such that the dilute (40–300 ppm) coloring metal ion is present in its reduced form (e.g. Au^+). Gold reduction has been accomplished historically by using Sn as a reducing agent, following the reaction:



However, the electrons needed for gold reduction may be provided by other redox reactions and even from external irradiation. The ruby-red color of the gold nanoparticles is due to a resonant absorption of photons during the excitation of surface plasmons within the nanoparticles. It is a typical example of quantum (electron) confinement effects observed when crystallites are smaller than the wavefunction of an electronic state. This color is often referred to as *striking* because it suddenly appears upon heating.

7.3 Photochromic Glasses

Photochromic glasses darken or change color when exposed to light or UV radiation, giving rise to a wide range of applications such as ophthalmic lenses, architectural or automotive glazing, information storage, and display devices [23]. A phenomenon that has found important practical applications in optics relies on the presence of silver halide particles of a few nm precipitated in the glass through an appropriate heat treatment. When the glass is exposed to near-UV visible light, a dark coloration rapidly appears but the glass lightens more slowly when returned to the dark. It is interesting that generally the glasses do not darken completely inside a car, because the car windows block some of the UV radiation needed for the photochromic reaction. Temperature effects are intriguing: the higher the temperature, the less dark photochromic glasses will be, as, conversely, photochromic glasses will take longer to regain their transparency under low ambient temperature.

Under exposure to light, Ag^+ is reduced into Ag^0 , the halogen ions acting as the reducing agent providing electrons for silver particle formation. This results in light absorption by the conduction electrons of metallic Ag over the entire visible range, giving a neutral coloration (Figure 14). Some sensitizers such as Cu^+ may be added to speed up the process, which act as an electron donor for Ag^+ . The limited diffusion of halogens in the glass at room temperature is at the origin of the reversibility of the process, needed by most uses of photochromic glasses. Halogens serve as sinks for electrons as Ag oxidation proceeds during the fading stage.

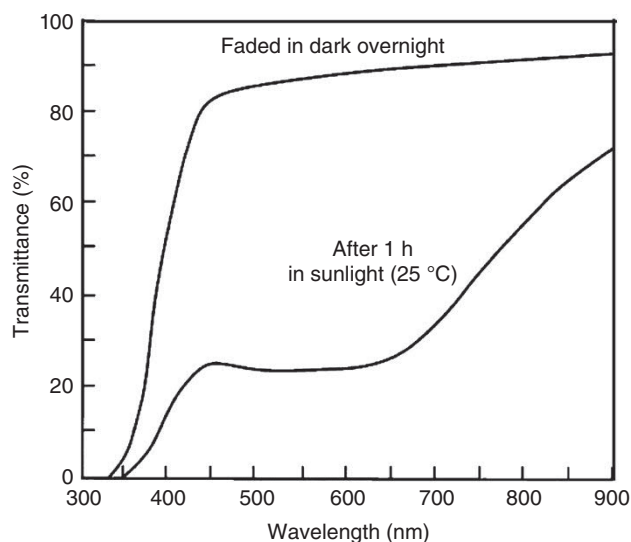


Figure 14 Transmittance curves for the crown glass used for Photogray Extra® photochromic lens in its lightened (faded) and darkened states. Source: After [23].

8 Perspectives

Light absorption by colored glasses remains an area that has great potential for development in many fields. Conversely, there is a continuous interest in ultrawhite glass for solar energy and data transmission applications, with the necessity to model the parasitic absorption caused by absorbing centers. The ability to modify the speciation of transition metal ions by modifying glass composition or melting conditions is an important advantage of glasses over crystalline matrices. The chemical dependence of the structure of oxide glasses, wherein transition metal ions occupy a large diversity of sites, opens the way for selecting specific environments that will impart original coloration. The chemical dependence of the geometry and relative proportion of the sites occupied by transition metal ions may sometimes be combined with an adjustment of the oxidation states as a function of synthesis conditions. This unique feature will continue to open the way to novel colors in glass materials.

Finally, regarding historical and cultural aspects (Ch. 10.6, 10.8), spectroscopic analyses may be used to improve our knowledge of ancient glassmaking technologies. Non-invasive portable spectrometers give information on the speciation of transition elements. The investigation of stained glasses from the 12th–13th centuries, which are blue colored by tetrahedral Co^{2+} , shows that more reducing conditions were achieved in medieval than in modern furnaces, enhancing the blue color by favoring Fe as Fe^{2+} and Cu and Mn as non-coloring

Cu^+ or weakly coloring Mn^{2+} , respectively [23]. The colorimetric analysis of stained glasses confirms the skills of medieval glassmakers to master redox kinetics and develop innovative glass colors.

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6.3

Photoluminescence in Glasses

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1 Introduction

Photoluminescence is an inelastic scattering process whereby a material subjected to optical illumination re-emits photons at the point of absorption [1]. The nature of the process has two important consequences: *scattering* means that the reemitted light diffuses into all directions, and *inelastic* means that the energy of the scattered photons changes. As a result, the observed wavelength also changes as does color if the process takes place in the visible range.

The phenomenon is striking in the peculiar *uranium glass*, which was most popular between the second half of the nineteenth and the first half of the twentieth century and is today found in antique shops in forms ranging from beads, vases, and plates to tableware and lampshades. Here, the strong photoluminescence gives rise to a characteristic greenish or even yellow color due to uranyl ions, UO_2^{2+} , in quantities of up to several thousands of ppm (Figure 1). Through exposure to sunlight (or, for better visibility, to an ultraviolet [UV] lamp), it can be readily distinguished from other glasses of similar color such as yellowish-brown uranate glasses (e.g. containing $\text{U}_2\text{O}_7^{2-}$), which are not luminescent. Also in practice, photoluminescence is routinely used to distinguish between the tin and airside of float glass (Chapter 1.4) because impurity divalent tin ions, Sn^{2+} , can be electronically excited by exposure to UV light: relaxation of this excited state back to the ground state occurs radiatively whereby a pale, bluish shine can be observed.

Today, however, the most important applications of photoluminescent glasses deal with optoelectronics. The purpose of this chapter is thus to review the basic physics that is needed to understand how such applications are designed. The fundamentals of photoluminescence and inelastic light scattering will first be presented. How glass chemistry can be engineered to optimize the phenomenon will then be described. Finally, key parameters such as quantum efficiency or emission lifetimes will be discussed.

In preamble, it may be useful to state how whether or not a certain glass exhibits visible or infrared photoluminescence can be determined from the electronic properties of its chemical components, in particular, of its minority species and dopants. Consider, for example, sodium oxide, Na_2O , an archetypal constituent of silicate glasses (Figure 2a). With eleven electrons, the sodium atom has the configuration $1s^2 2s^2 2p^6 3s^1 = [\text{Ne}]3s^1$. That is, one electron on the 3s orbital is only loosely bound and can thus be readily excited, for example, to 3p or other higher-lying states. In sodium gas, relaxation from 3p occurs through emission of a “yellow” photon according to the energy gap between the 3p and 3s states. This process is the basis for sodium-vapor gas discharge lamps (Figure 2b).

In glasses, however, sodium is clearly not incorporated in its atomic form, but in the oxidized Na^+ state in which the $3s^1$ electron is missing. The energy provided by visible (or UV) light is not sufficient to excite one of the deeper-lying 2s or 2p electrons so as to provide for photoluminescence. In contrast, X-rays can be employed for this purpose, which is why X-ray fluorescence is so commonly used for chemical analyses of glasses and other materials (Chapter 5.1). Obviously, weakly bound electrons are necessary, but not sufficient, to generate a visible photoluminescence in glass. These are available when the material contains Sn^{2+} , UO_2^{2+} or a multitude of other optically

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active ions within specific concentration limits. In their ionic form, some of the most prominent elements that may cause photoluminescence in glasses are summarized in Table 1. These are the transition metals, with their weakly bound outer d-electrons, and the rare earths. Among them the divalent manganese ion, Mn^{2+} ($[\text{Ar}] 3d^5$), is the most commonly involved in the photoluminescence of natural minerals and has also made its way into some artistic or decorative glass products, although less prominently, generating an attractive deep red-dish shine.



Figure 1 Photoluminescent glasses involving, from left to right, doping with Sm^{3+} , Eu^{2+} , Eu^{3+} , Pr^{3+} , Mn^{2+} , and UO_2^{2+} in various host glasses. Photograph taken under broadband ultraviolet (UV-A) irradiation.

2 Inelastic Light Scattering Through Photoluminescence

A beam of light with a wavelength appropriate for luminescence excitation can literally be seen, but at the specific color of luminescence, whereas this very same beam remains fully invisible in a neutral glass as long as there is no scattering toward the observer's eye. In Figure 3, a green (right, bottom) and a red (right, top) laser beam are guided through two blocks of transparent material. One (right) is a glass doped with ~ 500 ppm of trivalent europium, Eu^{3+} , and the other is a glass ceramic (Chapter 7.11) with a crystal size of ~ 30 nm and a crystal volume fraction of $\sim 80\%$. In the glass specimen, the green laser excites Eu^{3+} species to emit red (fluorescent) light, visible to the observer. The red laser beam is not seen because it is scattered neither inelastically nor elastically. In the glass ceramic specimen, both beams are scattered elastically at the glass–crystal interfaces although the red one is scattered to a lower extent because of its higher wavelength relative to the crystallite size.

Physically (Figure 4), photoluminescence in Eu^{3+} -containing glasses involves various sharp bands that result from the intra-configurational $4f \leftrightarrow 4f$ parity-forbidden electronic transitions from the Eu^{3+} excited state of $^5\text{D}_0$ to the states of $^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) (Figure 4c). As discussed later, the local structural environment does not notably affect the energetic location of the transitions since the involved f-levels are well shielded from the surrounding anions. The probability of certain relaxation reactions is strongly affected by the ligand symmetry, however, which represents a useful

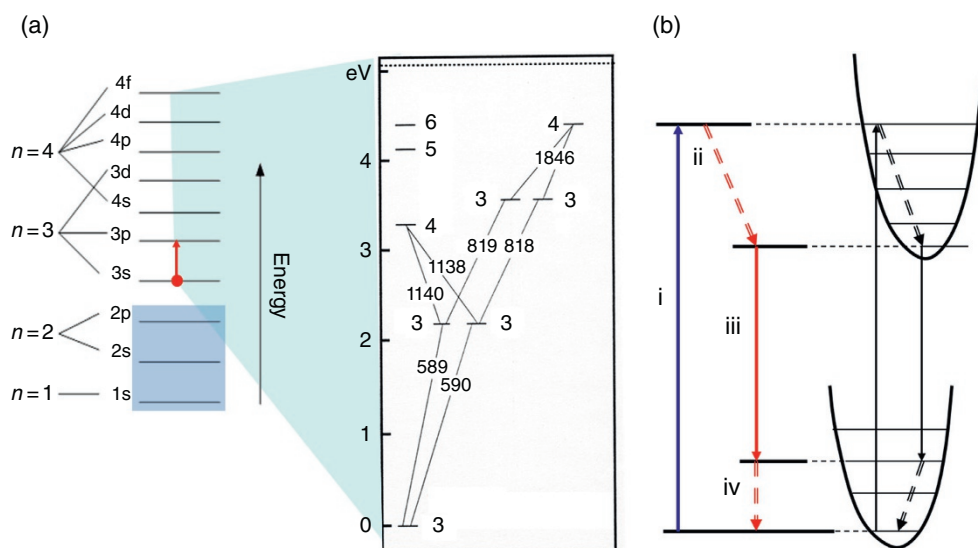


Figure 2 Electronic transitions in sodium. (a) Electronic configuration of atomic sodium, $[\text{Ne}]3s^1$, providing for a characteristic yellow luminescence. (b) Photoluminescence whereby an incoming photon creates a state of excitation (i), which relaxes non-radiatively through a series of narrow jumps until the emission level is reached (ii). From the emission level, relaxation occurs predominantly radiatively, i.e. through emission of a photon (iii) to a deeper-lying basin within which further non-radiative transitions may occur (iv).

Table 1 Electron configuration of some transition metal and rare earth elements.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
3d ²	3d ³	3d ⁵	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ¹⁰	3d ¹⁰			
4s ²	4s ²	4s ¹	4s ²	4s ²	4s ²	4s ²	4s ¹	4s ²			
Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
6s ²	6s ²	6s ²	6s ²	6s ²	6s ²	6s ²	6s ²	6s ²	6s ²	6s ²	6s ²
4f ¹ 5d ¹	4f ² 5d ¹	4f ³ 5d ¹	4f ⁵ 5d ¹	4f ⁷	4f ⁷ 5d ¹	4f ⁸ 5d ¹	4f ⁹ 5d ¹	4f ¹⁰ 5d ¹	4f ¹¹ 5d ¹	4f ¹² 5d ¹	4f ¹⁴
5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶	5s ² 5p ⁶

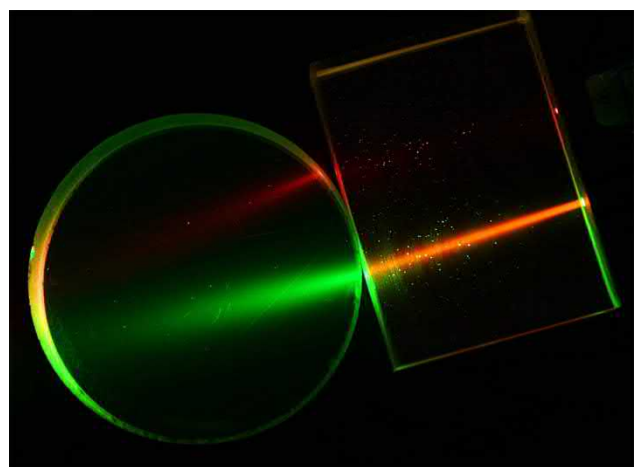


Figure 3 Elastic and inelastic scattering of red (top) and green (bottom) laser light through a block of Eu^{3+} -containing glass (right) and a transparent glass ceramics (left). A red photoluminescence is excited with green light only in the glass. Photograph taken under broadband ultraviolet (UV-A) irradiation. Individual bright spots caused by residual microbubbles in the glass specimen (See electronic version for color figures).

structural probe. Technical applications rely on the broad absorption band of Eu^{3+} in the 350–420 nm spectral region (Figure 4a), which makes Eu^{3+} (and its divalent counterpart) one of the most prominent optical activators in solid-state phosphors [2]. In this context, glasses as host materials offer potential advantages such as very high compositional flexibility, simple and low-cost manufacture, versatile forming technologies, superior thermal stability, and epoxy-free assembly processes. But these advantages usually go at the expense of the absorption cross section and quantum efficiency of luminescence, which results in potentially low quantum yield. Oxide glasses are, therefore, currently not used as phosphor materials.

There is a variety of photoluminescence schemes (Figure 5; see also [3]). Often depending on the desired material properties, glasses can be – at least in theory – tailored through different combinations of matrix glass

composition to which one, two, or more optically active species are added. In each case an incoming photon generates an excited electronic state before the ground state is recovered along a certain relaxation path that involves radiative and non-radiative transitions. The latter for example occur through energy transfer to the surrounding lattice by the creation of phonons, or through excitation of electrons of other optically active species. In the simplest case (Figure 5a), after excitation, part of the absorbed energy decays non-radiatively, and the remaining part causes the emission of a new photon. The energy of this new photon is always lower than that of the incoming photon, i.e. its wavelength is longer.

As an important extension of such a three-level system, the four-level system (Figure 5b) involves two non-radiative steps in between which the radiative transition is embedded. As discussed later, this case is especially relevant to laser-active materials because it allows for the so-called inversion of band occupation [4]. In some cases, a single photon of high energy may trigger the emission of two (or even more) secondary photons through a radiative cascade process (Figure 5c). This process presents an intriguing feature as it offers the possibility to enhance the quantum efficiency of the luminescence process to beyond 100 %. Vice versa, the excitation scheme can also be tailored, so two photons contribute to the excitation (Figure 5d). Materials offering such properties have been receiving much attention because they enable photons to be converted from lower (e.g. infrared) to higher energy through an *upconversion* process. Like two-photon process, however, upconversion suffers from a notoriously low efficiency.

In many cases, the absorbing and emitting ions are not the same [5]. For example, a sensitizing species can be used to ensure adequate absorption in a certain range of wavelengths (Figure 6). The absorbed energy is then transferred to a secondary dopant species, which provides the desired emission properties (Figure 5e). In a practical application, clearly the sensitizer and emitter must be

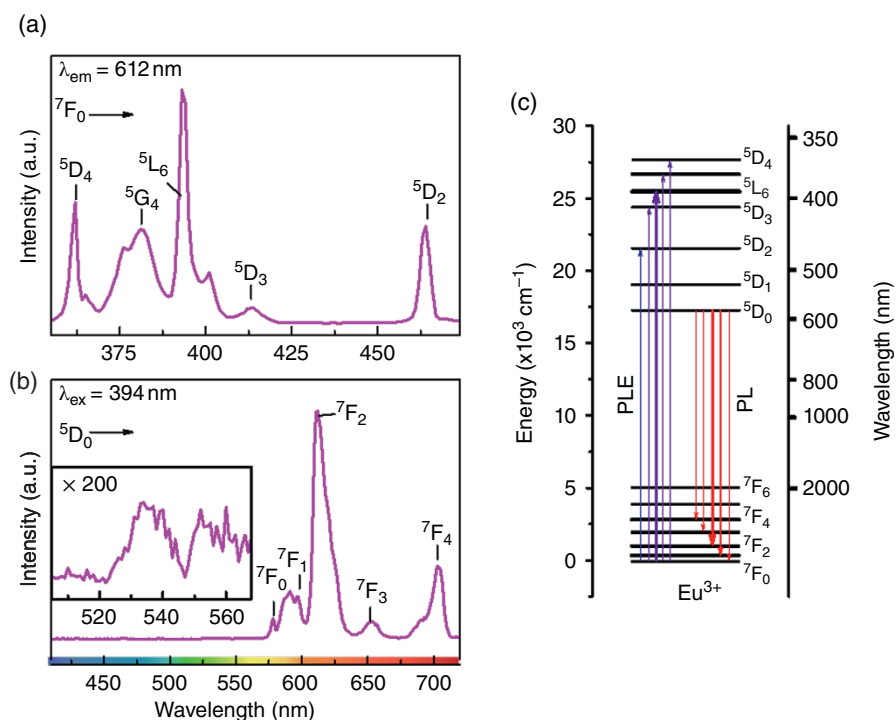


Figure 4 Spectral characteristics of photoluminescence from Eu^{3+} -doped glasses. (a) Typical excitation spectrum, with an emission band at 612 nm (cf. text). (b) Corresponding emission spectrum for excitation at 394 nm, including emission from higher-lying states (inset). Underlying energy level diagram given in (c).

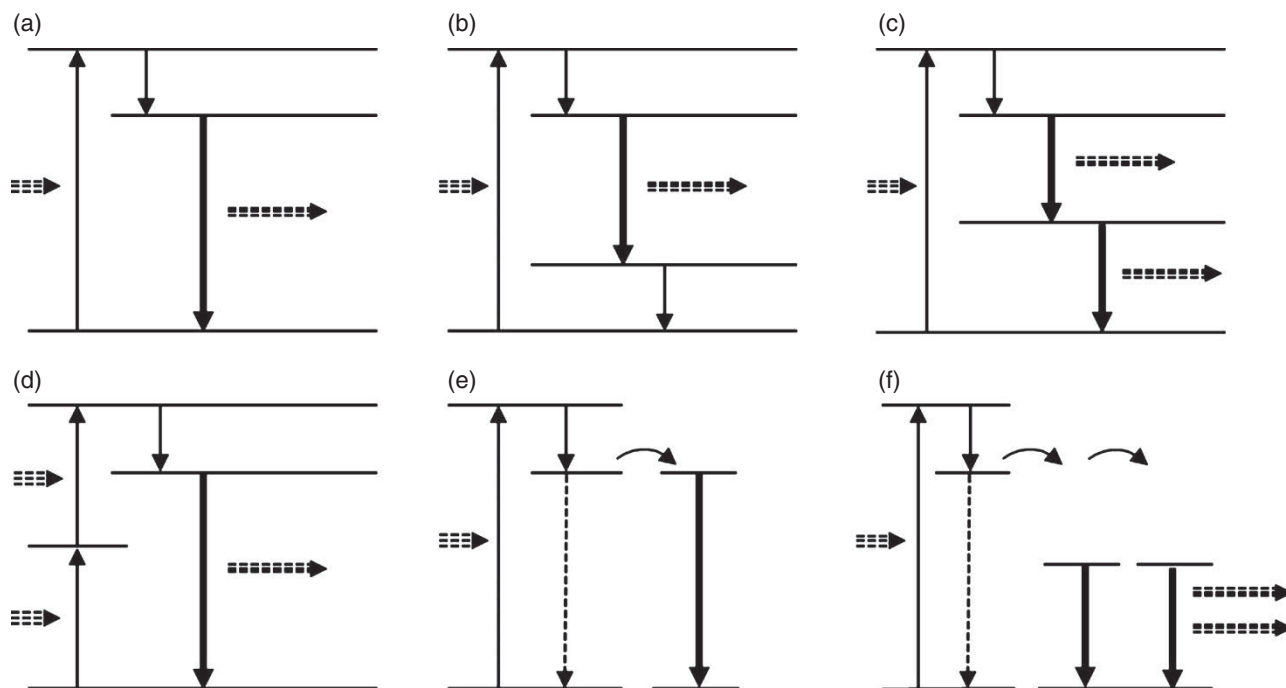
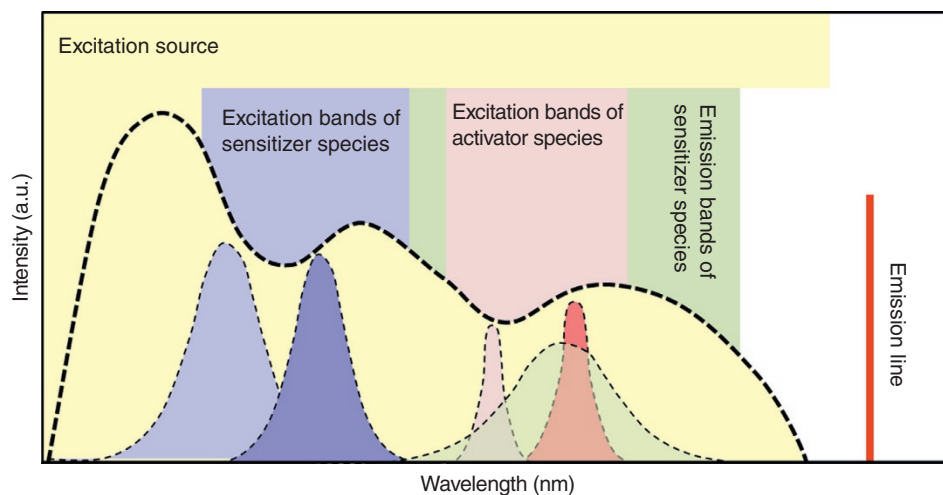


Figure 5 Different schemes of photoluminescence: (a) downconversion in a three-level system, (b) four-level system, (c) cascade emission, (d) upconversion, (e) energy transfer, and (f) quantum cutting.

Figure 6 Sensitization through co-doping: an efficient absorption in a certain spectral range is achieved through a suitable co-dopant species. From this species, the absorbed energy is transferred to the primary emitting species, thus increasing the range of spectral sensitivity of the latter.



chosen carefully on the basis of their electronic structures to ensure efficient energy transfer. If the excitation energy is high enough to be transferred to two or even more secondary emission centers, as done in cascade emission, an efficiency higher than unity can be obtained through the so-called quantum cutting (Figure 5f).

3 Photoluminescence and Glass Chemistry

The chemical design of photoluminescent glasses typically addresses two aspects: the choice of a proper ensemble of optical activators and the search for a suitable matrix material. The activator may be a single dopant at a given concentration or a combination of multiple dopants with different functions (sensitizer, amplifier, emission center, etc.; e.g. Figure 6). Here, the immediate parameters of interest are the spectroscopic properties, that is, the excitation and emission schemes, excited state lifetime, and quantum efficiency. Secondary parameters may, for instance, include the temperature dependence of photoemission, saturation effects and the power dependence of the emission intensity, or cross-reactions such as excited state or anti-Stokes emission.

All these properties depend on the matrix chemistry whose choice thus is also an important feature. Especially important in this respect is the ability of the glass matrix to dissolve the activator species at sufficiently high concentrations without triggering phase separation, clustering, or crystal nucleation. In addition, specific redox conditions are needed to stabilize the desired oxidation state (Chapter 5.6) and to secure the absence or specific presence of photooxidation or photoreduction reactions, whereas the matrix composition should ensure appropriate ligand configurations (ligand chemistry, crystal field

strength, coordination, and symmetry) and phonon energy (i.e. the possible avoidance of non-radiative relaxation that would counteract photoluminescence).

Typically, glass matrices with low phonon energy are sought, e.g. tellurites, fluorides, or fluorophosphates (cf. Chapter 6.5), in which non-radiative relaxation involves the concerted action of multiple phonons and, thus, becomes less and less probable. One should not disregard seemingly secondary glass properties, however, because in practice they may play a still more important role. For example, the possibility of fiber drawing largely relies on viscosity and liquidus temperature or on the absence of crystallization upon heating above the glass transition temperature (Chapter 6.5). The thermal expansion of the glass may become problematic in high power applications if it causes the formation of mechanical stress (Chapter 3.12). As for the refractive index, Abbe number, and thermal dispersion (Chapter 6.1), they determine the numerical aperture and thermal lensing effects during laser operation or the efficiency of light extraction. Finally, nonlinear optical effects determine the damage threshold for potential laser glasses. Because these features are discussed in other chapters, however, here the focus will be placed on the activator species and the resulting mechanism of photoluminescence.

Some typical elements that may play a role as activators or sensitizers in photoluminescent glasses have already been listed in Table 1. Like the sodium counterexample in the glass matrix (Figure 2), they are usually present in oxidized forms, i.e. with one or more of the outer electrons missing. The remaining electronic configuration determines the actual optoelectronic properties as already discussed for the archetypal case of Eu^{3+} (Figure 4). The origin of photoluminescence from the latter is an $f-f$ transition. As seen from Table 1, such a transition is shielded from the environment by the outer 6s orbital. A typical consequence is the very low dependence

of spectral band position on ligand situation, that is, matrix chemistry and activator coordination. The photoluminescence emission bands are, therefore, characteristically narrow as exemplified by Eu^{3+} -, Tb^{3+} -, or Er^{3+} -doped glasses. This feature is common among many of the rare earth activators in which f - f luminescence bands are observed. The excited state positions of the most relevant trivalent rare earth species are summarized in Figure 7. These cover the elements from cerium to ytterbium (with the exception of the unstable radioactive promethium, Pm^{3+}). In addition to the trivalent states, other oxidation states are also of importance in glassy materials for some rare earth elements, e.g. Eu^{2+} , Yb^{2+} , and Sm^{2+} . In tetravalent Ce^{4+} , all outer electrons are missing, so, as for Na^+ , neither color nor photoluminescence is typically observed. Although the latter species are not considered in this chapter, we note that not only f - f but also other types of transitions may occur, in particular, f - d , in such redox states.

Whereas the resonance energy of an f - f transition is typically independent on crystal field strength, the transition probability between some of the degenerate states depends on ligand symmetry through its effects on orbital distortion. As a result, the intensity ratio among certain emission peaks is a function of local symmetry. Hence, rare earth elements can be used as highly sensitive and extremely local structural probes, even in cases where other techniques such as X-ray diffraction fail to provide useful information. In addition to the f - f transitions, f - d or d - d transitions can be exploited in rare earth ions with lower valences or in transition metal ions. Here, splitting of the d -levels is strongly affected by the type and number of ligand species and, thus, matrix composition. In the

example of trivalent chromium in a phosphate glass matrix (Figure 8, [6]), Cr^{3+} has the electronic structure of $[\text{Ar}]3d^3$, that is, three electrons on the outer d -level. If Cr^{3+} is integrated into a solid matrix, interaction with the surrounding ligands leads to crystal field splitting. The degree of splitting depends on the strength of the crystal field, i.e. on the coordination number, symmetry, and type of anions. At a given field strength (Figure 8), a certain order and energetic position of all possible states is achieved. In the present case, the corresponding optical absorption spectrum is dominated by two broad absorption bands that are associated with the characteristic $^4A_2 \rightarrow ^4T_1$ and $^4A_2 \rightarrow ^4T_2$ transitions. A zoom on the red region reveals a further, weaker band corresponding to $^4A_2 \rightarrow ^2T_1$ and $^4A_2 \rightarrow ^2E$ transitions. Photoemission occurs in the near-infrared (NIR) spectral region.

The Tanabe–Sugano diagram is usually applied for a quantification of the effects of field strength on the electronic structure of d -elements [7]. It uses the Racah parameter B and a crystal field parameter, denoted D_q , to scale band energy and field strength. For Cr^{3+} (and also many other d -ions), an interesting question is that of the dependence of the lowest excited state (from which luminescence is expected) upon crystal field strength: here, one finds that an intermediate octahedral field of approximately $2.1 < D_q/B < 2.3$ typically separates the low and high field regions. Between those two regions, the emitting state is either 4T_2 or 2E , whereby only the 4T_2 state is very sensitive to D_q/B (Figure 8). When the Cr^{3+} ion locates in a weaker ligand field environment, the 4T_2 level is lower than the 2E level, which then results in a broad-band emission arising from the spin-allowed $^4T_2 \rightarrow ^4A_2$ transition. In contrast, when the Cr^{3+} ion locates in a

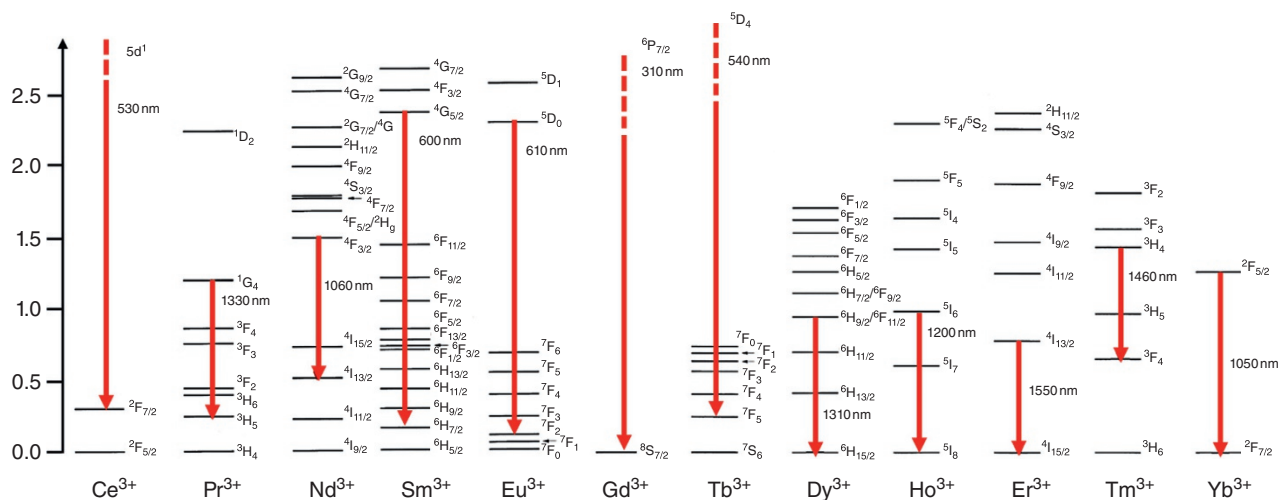


Figure 7 Excited state configuration of various trivalent rare earth ions. The arrows indicate some emission reactions that have received attention for NIR lasing activity or other purposes (labels indicate emission wavelength). Pm^{3+} , positioned between trivalent Nd and Sm, not shown.

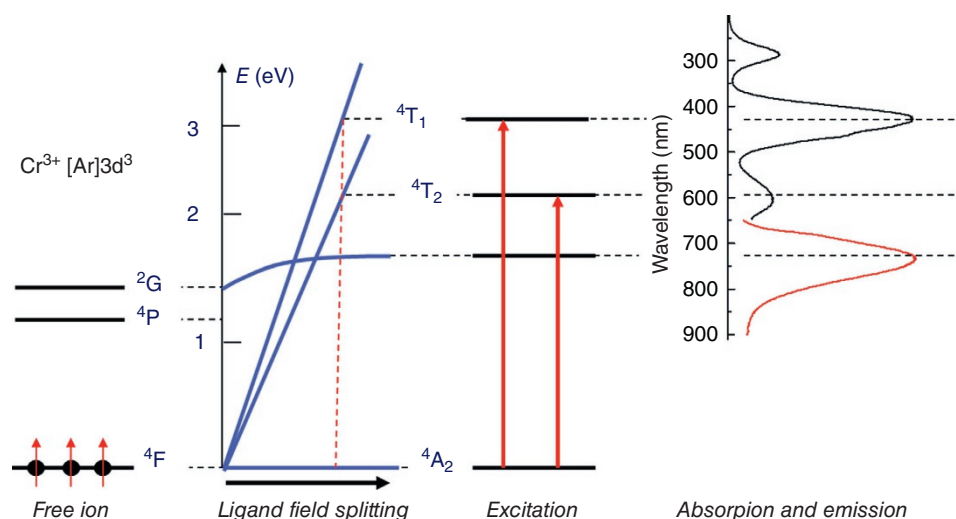


Figure 8 Photoluminescence from Cr^{3+} in a phosphate glass matrix (simplified). Depending on ligand field strength, ${}^4\text{T}_1$ and ${}^4\text{T}_2$ are split to different extent, which results in the characteristic variations in Cr^{3+} -related glass color. Photoluminescent reemission occurs from the lowest excited state.

strong crystal field, the ${}^2\text{E}$ level falls below the ${}^4\text{T}_2$ level, and, thus, the spectrum exhibits the sharp *R*-line originating in the spin-forbidden ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition (such as in the very prominent example of crystalline ruby lasers in which Cr^{3+} precipitates in the strong ligand field of Al_2O_3). Similar effects can be exploited in many of the d-element activator species for which the emission characteristics of a given redox state vary widely with the field strength.

Beyond very popular rare earth and transition metal ions, certain activator species have been reaching a level of significant research activity for application in glasses. Here, the most prominent recent example is bismuth in its various oxidation states (Figure 9). A major interest in this species was initiated by the discovery of broadband

photoluminescence in the NIR spectral region of Bi-doped silica glass [8]. Involving a broad variety of host glasses, subsequent studies have shown that this emission band covers the major part of the telecom spectral range, i.e. the range of wavelengths within which optical data are transmitted. For such data transmission, optical amplifiers are required to enable photoemission to be stimulated optically in the relevant spectral range. Today's benchmark material is the Er^{3+} -doped fiber amplifier (EDFA), which relies on the luminescence properties of trivalent erbium (Figure 7). It provides a unique set of properties, so it has an unchallenged efficiency in optical amplification around the $1.5\ \mu\text{m}$ spectral range [9]. This is also the range where vitreous silica fiber exhibits the lowest optical loss (Chapter 6.4), thus making it a perfect

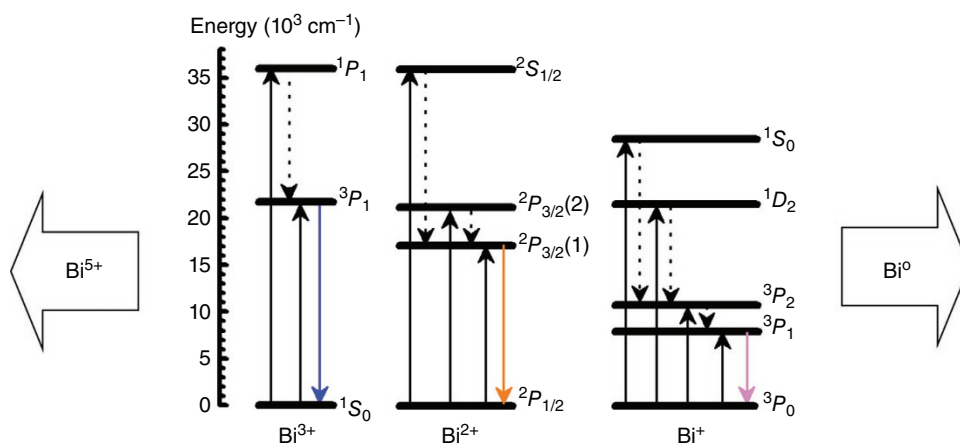


Figure 9 Simplified representation of the electronic states in some optically active ion species of bismuth.

match for long-range optical communication. But a problematic feature has been the limited spectral bandwidth yielded by the fundamental nature of the underlying f–f transitions in Er^{3+} . Here, the discovery of ultrabroad NIR emission from Bi-doped glasses has been considered as offering a promising alternative although technical demonstrations have not yet been successful. Interestingly, the fundamental origin of NIR photoemission from Bi-doped glasses remains highly debated [8].

Taking a broader look at bismuth in glasses, one notices that the multiplicity of redox states in which the bismuth ion (or ion cluster) may be present allows for a broad variety of materials with fundamentally different optical activities. In Figure 9, only the archetypal cases of Bi^{3+} , Bi^{2+} , and Bi^+ are shown. With decreasing number of electrons, the electronic band gap of these species increases, so photoluminescence occurs at increasingly high energy (low wavelength). In all three redox states, however, the transition energies depend very strongly on crystal field, so the emission properties are also highly matrix dependent. The most common form of bismuth in glasses is Bi^{3+} , which usually exhibits blue or green photoluminescence. Divalent Bi^{2+} , on the other hand, shows red photoemission. This contrast provides another glimpse at the rich nature of the general subject and at the enormous possibilities existing to generate a specific photoluminescence in an appropriate glass matrix.

4 Efficiency, Lifetime, and Quenching Effects

The *quantum efficiency* is a key parameter in many applications of photoluminescence. It is in addition fundamental to understand physically the underlying relaxation process that finally leads to photon emission. It describes the ratio between the numbers of emitted and absorbed photons, that is, the probability that absorption of one single photon actually causes the photoluminescent emission of a secondary photon. That this probability is by definition lower than unity signifies that the relaxation scheme of Figure 2b represents only an ideal case: coexisting with photon emission (*radiative decay*), other relaxation pathways may be followed, in particular phonon excitation or energy transfer.

An accurate determination of quantum efficiency is not obvious. If conducted directly, it comprises determination of the absolute photon flux upon excitation and emission. Integration spheres and careful referencing are required for this purpose. The experimental approach then distinguishes between internal and external quantum efficiency, whereby the latter acknowledges the

existence of secondary effects such as the efficiency of light extraction or the occurrence of reabsorption, which also leads to a reduction in the experimentally visible intensity of photoluminescence. Efforts on materials development, therefore, often aim at increasing the external quantum efficiency.

In the specific case of glasses, however, the sole notion of quantum efficiency is often misleading in terms of practical applications because it does not provide a measure of the generated emission gain. In other words, high quantum efficiency does not guarantee high emission intensity. Regarding this parameter, the absorption cross section must also be considered so that the figure of merit is a convolution of quantum efficiency and absorption probability. Typically, this is where glasses suffer from a major drawback, i.e. they often have comparably low absorption cross section. In addition, common strategies for overcoming this problem such as increasing light–matter interaction pathlengths through multiple scattering cannot be employed because of the lack of a microstructure. On the other hand, one can increase the emission intensity either by increasing the amount of dopant or by directly enhancing the optical pathlength within the material. For both routes, glasses are particularly suitable: they can be chemically tailored to maximize the solubility of the optical activator and/or secondary dopant species, and they can be formed practically universally into any shape. In particular, in the form of optical fiber, they guarantee a maximum optical pathlength, which then often enables efficient photoluminescence even at low absorption cross sections.

Regarding the increase in dopant concentration, however, solubility is not the only requirement. The maximum dopant concentration is usually limited by the occurrence of energy transfer reactions, often denoted *concentration quenching*. Such reactions may occur over short or long spatial ranges (e.g. Foerster transfer, Dexter transfer) and always reduce quantum efficiency. The maximum dopant concentration at which the drop in quantum efficiency is observed is termed the *critical concentration*, x_c .

Some simplistic formulas have been constructed to aid in the approximate quantification of energy transfer probabilities. For example, the critical distance R_c , representing the mean spatial separation between two emission centers at x_c , is often estimated from

$$R_c = \sqrt[3]{\frac{6V}{\pi x_c N}}, \quad (1)$$

where N is the number of emission sites per unit volume V (usually taking the volume and number of sites of a unit cell for crystalline materials and the molar volume and

molar concentration for glasses). For electric dipole–dipole interactions, R_c is sometimes also estimated directly from the excitation and emission spectra:

$$R_c^6 = \frac{3 \times 10^{12} \times f}{E^4} \int f(E)F(E)dE, \quad (2)$$

where f is the oscillator strength and E the energy of maximum spectral overlap and where the integral represents the overlap of the normalized emission and excitation spectra.

In a more detailed consideration of glass structure, however, the value of R_c has only little meaning because spatial relations among the atomic constituents of the glass network are determined by bond lengths, coordination numbers, and bond angles. Especially over short ranges, they cannot be approximated through simple mean-field statistics. Instead, one may calculate the probability of cluster formation across first, second, or third coordination shells, which is approximately derived from the molar concentration of the specific ion, its coordination number, and the coordination numbers of all other anionic and cationic constituents of the system.

In many cases, an analysis of the lifetime of photoluminescence is a more suitable way to judge the probability of radiative relaxation. In a first approximation, a simple exponential relaxation function is often used to describe the rate at which the emission level is depopulated:

$$I(t) = A \exp\left(\frac{-t}{\tau}\right), \quad (3)$$

where τ is the decay time and A is a fit constant. This law assumes that the transition probability is independent of the population of the excited state. In certain cases, which are not considered here, stretched or compressed exponentials are observed instead. The value of τ represents the time after which the initial emission intensity has decreased to a fraction of $1/e$. Non-radiative relaxation occurs very rapidly through phonon activation, in particular in narrow energy quanta, so the experimentally observed lifetime of photoluminescence is decreasing with increasing non-radiative contributions. In such a case, one can decrease the probability of non-radiative relaxation by either decreasing the temperature or by increasing the number of phonons that need to be activated collectively in order to bridge the respective energy gap between the excited and ground states. This is why glasses with low phonon energy are typically sought as host species. In the theoretical case of absolute zero temperature, no phonon relaxation would occur, which would ensure a maximum lifetime in the absence of phonons. Therefore, observing the emission lifetime as a function of dopant concentration (or other chemical variations on the system) always provides some relative

information on quantum efficiency. One then uses a temperature-dependent lifetime analysis to extrapolate this information so as to obtain also absolute data, for instance, by referencing the observed lifetime to its extrapolated value at absolute zero temperature.

One can also treat electronic energy transfer processes in this way, for example, by approximating the energy transfer efficiency η_{ET} with

$$\eta_{ET} = \frac{1 - \tau_s}{\tau_{s0}}, \quad (4)$$

where τ_{s0} and τ_s represent the values of emission lifetime from an activator species in the absence and in the presence of a secondary energy acceptor species, respectively. The energy transfer rate κ_{ET} between the two entities can also be estimated:

$$\frac{1}{\tau_s} = \frac{1}{\tau_{s0}} + \kappa_{ET}. \quad (5)$$

Such considerations often provide practical tools for exploiting or avoiding energy transfer processes by chemical tailoring.

5 Applications

Because of their emission gain and other spectroscopic properties, photoluminescent glasses do not play an important role in prominent applications such as phosphors in solid-state lighting or display. But they did find niches as irreplaceable components in various specialty sectors among which optically active fiber devices and glass lasers are the most important [10, 11]. And, from a chemical standpoint, another important application of glass photoluminescence concerns probing of short-range structural features through the aforementioned dependence of spectroscopic properties on the ligand field in the vicinity of the active species. In particular for the d–d or f–d transitions, knowledge of the variation of band structure as a function of field strength (such as given in Tanabe–Sugano diagrams) enables the crystal field strength to be directly evaluated from the peak positions of the observed emission bands. For example, this allows the local energy density to be probed or bond distance and coordination number to be determined by comparisons with reference materials (Figure 8). In a less direct way, analysis of f–f transitions provides information of ligand symmetry. As a final perspective, the study of energy transfer may help to shed light also on longer-ranging structural features, including clustering and non-random ion precipitation.

Table 2 Prominent examples of laser-active glasses.

Lasing species	Laser line (μm)	Glass matrix
Er^{3+}	1.5	Fluorophosphates
Ho^{3+}	1.9	Silicate
Nd^{3+}	0.9	(Na, Ca) aluminosilicate
	1.1	(K, Ba) silicate
	1.4	(La, Ba, Th) borate
Tb^{3+}	0.54	Borate
Tm^{3+}	1.9	(Mg, Ca, Li) aluminosilicate
Yb^{3+}	1.0	(Mg, Ca, Li) aluminosilicate

Table 3 Sensitizer–activator combinations in some laser glasses.

Lasing species	Sensitizer species	Glass matrix	Molar ratio of activators	Emission peak (μm)
Er^{3+}	Yb^{3+}	Fluorophosphate	1 : 8	1.5
Ho^{3+}	Yb^{3+}	Silicate	1 : 1	1.9
Nd^{3+}	Mn^{2+}	Phosphate	1 : 1	1.1
Tm^{3+}	$\text{Yb}^{3+}, \text{Er}^{3+}$	Silicate	1 : 1	2.0
Yb^{3+}	Nd^{3+}	Borate	1 : 1	1.0

The technical applications of active optical fiber and bulk laser glasses are dominated by rare earth-doped materials. Some prominent examples are given in Table 2. The popular Nd^{3+} -doped glass lasers involve commercial products such as codes LG 660, LG 670, LG 680 (all Schott, Germany), LSG 91H (Hoya, Japan), or Q246 (Kigre, USA). Common to all laser glasses, they exhibit emission lifetimes above 500 μs (ideally at room temperature, occasionally at cryogenic temperature), sometimes reaching up to several ms such as in Er^{3+} -based systems. Typical combinations of sensitizer and activator are listed in Table 3. With the exception of Mn^{2+} in Nd^{3+} phosphate laser glasses, here as well, rare earth sensitizers are dominating.

Beyond bulk laser glasses, vitreous silica remains the most important material for optical fiber thanks to its well-established high-purity processing schemes and the underlying materials logistics (Chapter 6.4). Consequently, optically active fiber relies on rare earth-doped silica. The dopants includes Er^{3+} for telecom fiber amplifiers [12], Yb^{3+} for high power lasers [13], and further species analogous to those shown in Table 2 for the farther infrared [14].

6 Perspectives

Photoluminescence is a peculiar phenomenon that unfolds particular beauty in glasses. *Shining from within*, this very attractive visual effect results from the combination of inelastic scattering and optical transparency and may be put to use in many ways in art and design, consumer glass products, fluorescent glazes and enamels, or fiber-illumination sources, which are beyond the scope of this chapter. But glasses are not always ideal materials for more technical applications, in particular, when one needs high emission gain, high absorption cross section, elastic scattering and light diffusion, or color quality and stability. In some niches such as optical fibers, however, luminescent glasses have become indispensable materials. Here, exploitation of the emission and excitation properties of transition metal dopants and other optically active species beyond the rare earths remains a field of challenge. In other, more exploratory areas, interesting devices, and design studies continue to evolve, including luminescent concentrators, light-emitting fibers, or three-dimensional displays.

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6.4

Optical Fibers

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1 Introduction

Whether in physical or biblical contexts, light has been illuminating the universe since its beginnings. As reviewed in Chapter 10.10, the first substantive scholarly efforts at describing light can be attributed to Euclid of Alexandria (*Optica*; ca 300 BC), Claudius Ptolemy (*Optica*, ca 150 AD), and later to such luminaries as Abū ‘Alī al-Ḥasan ibn al-Haytham (*Book of Optics* written in the 1010s), René Descartes (*Dioptrique* in 1637), Robert Hooke (*Micrographia* in 1665), Isaac Newton (*Opticks* in 1704), and James Clerk Maxwell (*A Treatise on Electricity and Magnetism* in 1873). Indeed the millennial anniversary of Ibn al-Haytham’s opus was one of several reasons for 2015 being celebrated globally as UNESCO’s *International Year of Light*.

As relates to optical fiber, the operative principle governing light confinement and propagation is that of total internal reflection taken in a ray-optic construction. Total internal reflection was first described by Johannes Kepler in 1611, mathematically described by Willebrord Snellius (1580–1626), and eventually popularized in the mid-nineteenth century through the giant luminous fountains invented by Jean-Daniel Colladon [1] on the basis of total reflection of light at the air–water interface (Figure 1). Even though the same phenomena were observed at the same time in meter-long bent rods drawn from crown glass by Jacques Babinet [2], the potential of optical fiber would still not be more fully appreciated for nearly another century. Not until,

that is, the advent of the laser as a coherent and collimated light source and the description of materials and loss mechanisms in waveguides at optical frequencies [3]. The latter work earned Charles Kao the Nobel Prize in Physics in 2009 for “groundbreaking achievements concerning the transmission of light in fibers for optical communication.”

A global race ensued to develop optical fiber with sufficiently low loss such that (laser) light could efficiently propagate over long distances and enable high-speed and high-capacity communications. As detailed below, these goals required, at least as relates to the glasses, a wide variety of innovations that included optimized glass compositions, glass and fiber fabrication processes, and light-amplifying and optically nonlinear fibers, the specifics of which are all application specific. Though applications do abound, some of which are described below, the present and near future use of glass optical fibers remain dominated by telecommunications, at least on a volume basis. For this reason, this chapter will largely focus on the glasses and processes associated with communications. At the time of the printing of this *Encyclopedia*, the global production of optical fiber for communications exceeds 10 m per year for every person on Earth.

The performance of an optical fiber most strongly depends on the optical properties of the constituent glasses and on the design of the fiber itself. These topics will be described first, without delving into other thermal, mechanical, or chemical properties of practical interest that are adequately dealt with in other chapters. The most common glass families employed in making practical optical properties are then discussed before the main fabrication processes used are reviewed. Finally, a variety of applications of optical fibers are briefly presented.

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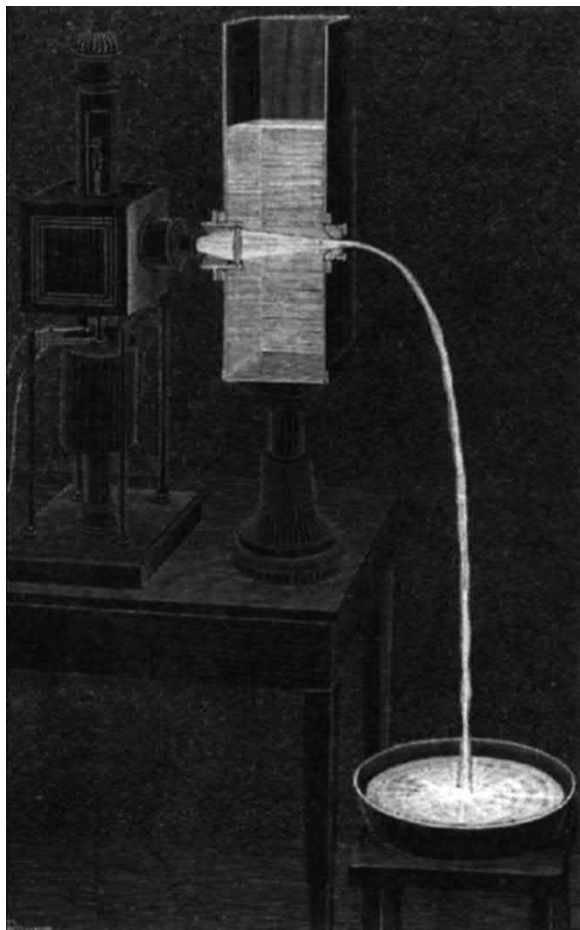


Figure 1 Colladon's experiment with flowing water as a waveguide [1].

2 Optical Properties and Fiber Designs

2.1 Optical Properties

2.1.1 Dispersion, Absorption and Scattering

The vast majority of optical fibers are passive in that they serve as hair-thin conduits that simply transmit light from one place to another. As with any property, the efficiency with which fibers perform this task depends upon both intrinsic and extrinsic factors. Given the maturity of optical fiber fabrication, extrinsic factors such as bubbles, striations, and inclusions will be neglected. Impurities, however, are critical impediments since they absorb light in a way that can have great impact on long-distance communication links. Given the spectral bands of significance for the primary optical-fiber applications, the most detrimental impurities tend to be hydroxyl groups, $-OH$, and transition metals, most notably iron (Fe^{2+}) and copper (Cu^{2+}).

Intrinsically, the canonical optical property of any material is the index of refraction (cf. Chapter 6.1). It is a relative measure of the speed of light in vacuum, c , to that in the material, v , such that $n = c/v$. Macroscopically, a general expression for the refractive index can be derived from the Newtonian dynamics of a mass/spring system under the influence of an applied field (i.e. the electric field of light). The electric field intensity of light varies as a sinusoid in time (and position), and so the dielectric displacement of the charged species within the glass follows this polarization. At optical frequencies, the relevant charged species that define the properties of optical fiber are the electrons (in the ultraviolet) and the ions/molecules (in the infrared). Further details on the macroscopic derivation of the refractive index can be found in any introductory optics or optical materials text [4].

Since the polarization of the electrons and/or ions is frequency dependent, so is the refractive index: this dependence of index upon frequency or wavelength (λ) is called the chromatic dispersion. Though not the focus of this Chapter, it is an important consideration in telecommunication optical fibers since data signals are composed of a small range of wavelengths. Since each wavelength experiences a slightly different refractive index, hence velocity, the signals spread over time (distance) and can ultimately overlap such that information is lost. For this reason, early systems were designed to work at the zero dispersion point, which for silica glass optical fibers is at a wavelength of about $1.3\ \mu m$ [4, 5]. Microstructured and photonic crystal optical fibers possess dispersion properties that can be tailored via specific fiber design (Figure 2). This latter point is useful since the waveguiding properties, such as loss and dispersion, of an optical fiber depend both on the materials from which it is made as well the waveguide design itself.

Within the spectral bands of conventional (bulk) optics, the refractive index of conventional glasses and optical fibers decreases with increasing wavelength (normal dispersion). As the interaction between the electric field of the light and the charged species is one of a damped resonance, there are frequencies or wavelengths where dielectric relaxation is approached. At this frequency, the dispersion becomes anomalous, and the glass becomes highly absorptive. The reason is that the refractive index is a complex function whose real part is what is typically thought of as the index of refraction and the imaginary part the absorption. Accordingly, since the refractive index changes with wavelength, so too does the absorption or, more importantly for optical fibers, the absorption per unit distance, called the attenuation (typically given in units of dB/km).

As noted, absorption caused by electrons and ions/molecules occurs in the ultraviolet and mid-infrared

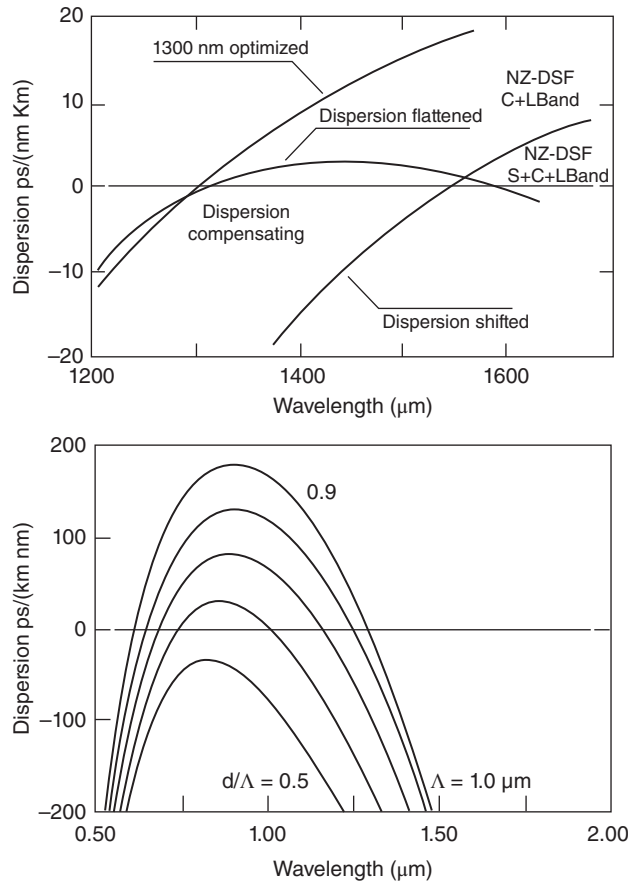


Figure 2 Dispersion curves for silica (top) and for selected MOF/PCF fibers (bottom). Source: Reprinted with permission from [5].

ranges, respectively. In between, i.e. in the visible and near-infrared, glasses are intrinsically transparent and have potentially low attenuation. This feature is especially useful for long-haul, fiber-based telecommunication systems since the greater the distance light can travel through a fiber, the fewer amplifiers are needed to ensure that the optical signals arrive at their destination, the result being a simpler and less costly system. In addition to absorption, light can also be partially scattered by minute density fluctuations in the glass. Given that the size of the structural units causing the scattering is very small compared with the wavelength of light, the process at work is Rayleigh scattering with an intensity that depends on wavelength as λ^{-4} . The process is generally considered a source of attenuation for transmission by a fiber over a given distance because the light can be redirected even though it is not absorbed owing to the elastic nature of the scattering.

Accordingly, the intrinsic transparency of a glass optical fiber is defined by the absorption of electrons in the ultraviolet, Rayleigh scattering in the visible and near-infrared, and absorption by ions/molecules in the

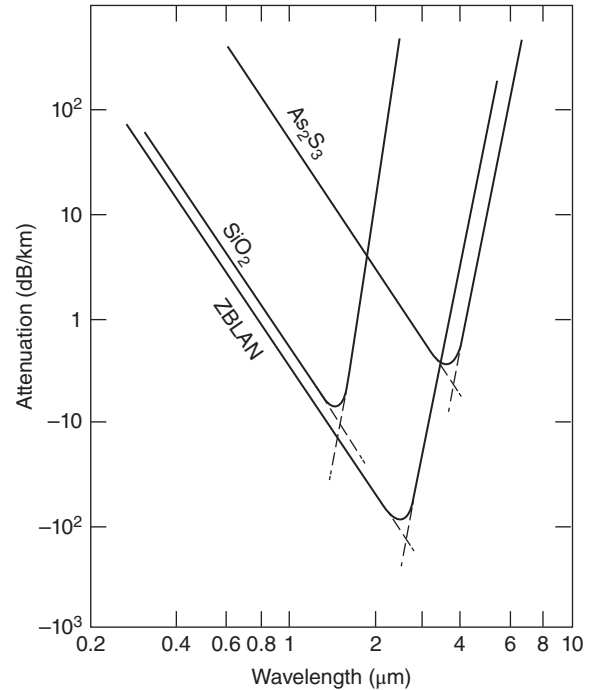


Figure 3 “V-curves” of theoretical attenuation as a function of wavelength for selected optical fiber materials.

mid-infrared, which differs for each glass composition. A plot of loss as a function of wavelength yields a “V-curve,” so designated from the shape of the curve (Figure 3). Because of the maturity of the chemical vapor deposition process, the lowest loss optical fiber realized to date remains conventional telecommunication-grade silica.

2.1.2 Active Optical Properties

Though quite a few ions can generate light upon suitable excitation when doped into glass, the rare earths are the most commonly used because their $4f$ electrons yield efficient and narrow linewidth emissions thanks to their efficient shielding by outer lying $5d$ states. The amorphous structure of glass promotes inhomogeneous broadening of the rare earth dopant absorption and emission lines, however, which was originally thought to preclude the possibility of laser action. But the concern proved to be wrong as it was not long after that the first experimental realization of lasing by T.H. Maiman in 1960 with ruby ($\text{Cr}^{3+} : \text{Al}_2\text{O}_3$) and the first glass-based laser were reported [6].

This first glass laser employed neodymium (Nd^{3+}) as the active dopant in a barium crown glass (N.B. a dopant is a small but important value-added constituent to the composition, whereas the presence of an impurity generally is unintended and unwanted). Since then, virtually all of the rare earth ions have been made to lase [7].

The glass host plays a critical role in determining which transition, hence wavelength, is involved and how efficient the laser action is. To first order, selection of the active dopant is based on the separation of its energy levels and on whether this difference is equivalent to the energy of the desired emission. Electrons from the ion's ground state are excited into the necessary state via optical pumping of light. The energy of this optical pump is resonant either with the excited state from which the emission occurs or with an excited state of energy higher than it, followed by relaxation into the desired excited state. Admixing of opposite parity states breaks the symmetry restrictions that would otherwise preclude emission from intra- $4f$ transitions: as such, the rare earths are considered weakly coupled to the host. The benefit of this weak coupling is the aforementioned narrow spectral linewidths as well as the possibility for fairly long-lived electron populations in the excited states prior to de-excitation. These excited state lifetimes, which can be of the order of micro-, through several milli-seconds, provide a metastability that facilitates the population inversion central to lasing.

An electron in a metastable excited state will de-excite either radiatively or non-radiatively. Without external stimulus, the relaxation is spontaneous in the former (light-emissive) case. With an external stimulus, which would most likely be a photon for dielectric glasses, then the relaxation is stimulated provided that the photon has an energy equal to the energy difference between the populated excited state and a lower lying level. For spontaneous emissions, the light given off has no correlation in direction, polarization, or phase to any other spontaneous emissions that may occur within the host at the same time, and its energy is the difference between those of the originating and terminal electron levels. For stimulated emission, the generated photon is, in contrast, identical in all ways (direction, energy, polarization, and phase) to the photon that stimulated it. This creation of equivalent photons is a hallmark of the laser process.

Further, if the stimulating and stimulated emissions are permitted to leave the host after a single pass, then the process is considered as optical amplification. If the stimulating and stimulated emissions are fed back into the host via some reflective structure in order to intensify further, then one denotes this an oscillator. Both amplifiers and oscillators are forms of lasers. The glass host is critical in the efficiency of the laser for several reasons. First, lasing requires gain that cannot apply until sufficient light is provided to offset losses, such as those from impurities or scattering sites. Accordingly, laser glasses and fibers should be of highest transparency, hence purity and homogeneity. Second, in addition to fundamental properties associated with the specific transitions of each rare earth, the so-called selection rules, the probability for a

radiative relaxation scales super-linearly with the refractive index of the host. In other words, all other things being equal, the most efficient laser hosts are glasses with the highest refractive indices.

In the case of non-radiative relaxation of the excited state electrons, heat is generated rather than light. Here host phonons stimulate the de-excitation and creation of additional phonons. As such, the host glass composition is of great consequence since the interatomic bonds, and their structural arrangement, determine the phonon spectrum. Of particular importance is the highest energy (longitudinal optical, LO) vibrational modes since they involve the phonons most responsible for facilitating non-radiative relaxation. In order to reduce non-radiative relaxations, glasses can be cooled since the phonon occupancy number (number of phonons of given energy) depends on temperature and follows Bose–Einstein statistics. Alternatively, glasses with heavier and more weakly bound atoms/ions would possess lower phonon energies and therefore would exhibit reduced non-radiative relaxation rates. More specifically, heavy metal oxides, fluorides, and chalcogenides would therefore be more radiatively efficient than conventional silica-based glasses, all other things being equal.

The glass composition has yet another influence on the active performance of optical-fiber amplifiers and lasers. Whereas it would normally stand to reason that more light-emissive dopant would yield more light, there is an optimum concentration for the rare earth dopant in a given glass. There are principally two reasons for this. The first relates to glass stability. Whereas phosphate and fluoride glasses tend to be highly multicomponent, and therefore more amenable to higher concentrations of any one species, most other conventional glass families – and particularly the silicates – generally have a fairly low “solubility” for rare earth ions prior to liquid–liquid immiscibility and phase separation. Other species, most commonly alumina (Al_2O_3), are added to reduce the immiscibility range (Chapter 5.2) and permit a greater concentration of rare earth dopants into the silica.

The second reason for an optimum concentration of rare earths is the phenomenon called concentration quenching whereby electrons from one dopant can interact with electrons and energy levels of a second dopant if said dopants are in reasonably close proximity; this happens to a greater extent probabilistically as doping concentrations increase. In the specific case of concentration quenching, excited state electrons move from dopant to dopant until, as is likely, they encounter an impurity, are absorbed, and can no longer contribute to the generation of light. In order to determine the concentration-quenching limit, the radiative lifetime of a given transition is measured as a function of dopant level in a given glass. The lifetime will remain constant until the

quenching limit is reached and the lifetime will rapidly decrease with any further increase in concentration. The ideal composition for most amplifier and laser applications is where the lifetimes are the longest just before the onset of quenching. Other ion-ion interactions may also take place at higher concentrations, including cross-relaxation and cooperative upconversion which can be either detrimental or actually useful in certain applications. For example, the cross-relaxation of thulium (Tm^{3+}) in silica at concentrations in excess of about 4 wt % permits quite efficient emissions at a wavelength of 2 μm when this ion is pumped at a wavelength of about 780 nm. Thulium-doped fiber lasers have exceeded 1 kW in output power, and the 2 μm is considered “eye-safer” for defense applications.

As with the first glass laser, the first optical fiber amplifier employed Nd^{3+} as the active dopant. A critical breakthrough occurred 25 years later when an optical fiber based on erbium (Er^{3+}) doped into silica was realized [8]. The importance of this finding was that Er^{3+} can efficiently amplify light in the 1550 nm range, which overlaps the aforementioned minimum attenuation spectral window for silica optical fibers. Hence erbium-doped fiber amplifiers (EDFAs) provided a means to boost all-optical signals in low-loss silica optical fibers and helped usher in global communications as it is known today.

A comprehensive compilation on various rare earth-doped fiber-based optical amplifiers and lasers is provided in [7]. Additionally, [9] reviews fiber- (hence glass-) based lasers for high-power (>1 kW) applications where additional complexities and systems-level considerations exist. The demands on the robustness of the glass and structure and performance of the resultant fiber are accordingly significant.

2.1.3 Nonlinear Optical Properties

Generally speaking, the previously discussed passive and active optical properties of glasses are termed linear phenomena because a linear relationship exists between cause and effect. For example, a change in the pump power incident on a glass laser will result in a linear change in the output power. The ratio of input to output is almost never unity owing to losses and inefficiencies in the system, but the changes generally are linearly related. Nonlinear effects are, in contrast, defined as ones where changes between input and output are not linearly related. With specific regard to optics, nonlinear optical properties derive from the same macroscopic mass/spring consideration as linear optics, but higher-order terms are included to account for real anharmonicity in interatomic bonds.

The refractive index, or, more appropriately, the dielectric susceptibility, is expanded as a power series in electric field as $\mathbf{P}_i(t) = \epsilon_o(\chi_{ij}^{(1)}\mathbf{E}_j(t) + \chi_{ijk}^{(2)}\mathbf{E}_j(t)\mathbf{E}_k(t) + \chi_{ijkl}^{(3)}\mathbf{E}_j(t)$

$\mathbf{E}_k(t)\mathbf{E}_l(t) + \dots)$, where $\mathbf{P}$ is the polarization (dipole moment per unit volume) vector as a function of time, t , driven by the electric field, $\mathbf{E}(t)$, vector of the light. The $\chi^{(n)}$ values are the linear ($n = 1$) and nonlinear ($n > 1$) susceptibilities. The linear refractive index, n , is related to the linear susceptibility as $n = (1 + \chi^{(1)})^{1/2}$. The amorphous structure of glass precludes even-order nonlinearities for reasons of symmetry though they can be present in acentric crystals. Accordingly, the polarization as a function of electric field given above can be recast in terms of refractive index, n . For glasses this is given by $n = n_o + n_2I$, where n_o is the linear refractive index, n_2 is the nonlinear refractive index, and I is the intensity of the light, which is proportional to $\mathbf{E}^2(t)$.

The more common nonlinear optical phenomena present in glass optical fibers include frequency-mixing processes such as third-harmonic generation (THG), sum-frequency generation (SFG), difference-frequency generation (DFG), optical-parametric amplification (OPA), and other nonlinear processes, such as the optical Kerr effect, self-focusing, self-phase modulation (SPM), optical solitons, cross-phase modulation (XPM), four-wave mixing (FWM), stimulated Raman scattering (SRS), stimulated Brillouin scattering (SBS), and multi-photon absorption.

Even in their earliest days, optical fibers provided a practical proving ground for understanding and utilizing nonlinear optical phenomena. The reason is that optical fibers possess two key attributes of value to nonlinear optics: long lengths over which weak effects can grow in magnitude and small core sizes that confine the light in a reduced cross-sectional area, thus greatly increasing the optical intensity (power per unit area). Interestingly, whereas nonlinear features were originally considered to be parasitic, Stolen [10] noted with respect to modern communication systems that “Fiber nonlinear optics has grown from a novel medium for the study of nonlinear optical effects, through a period where these effects appeared as system impairments, to the present day where optical nonlinearities are an integral part of high-capacity optical systems”.

2.2 Optical Fiber Designs

As a general rule, fibers are cylindrical structures whose lengths greatly exceeds their diameters. For conventional (e.g. telecommunications) optical fibers, lengths can range from meters, as for data centers, to thousands of kilometers, as in transoceanic cables. In these cases, the diameters are prescribed by convention as having an outer cladding glass diameter of 125 μm and a core diameter that depends on whether or not only a single waveguide mode propagates (core diameters of about 8 μm with numerical aperture of about 0.14 for typical communication wavelengths) or multiple ones do (core diameter

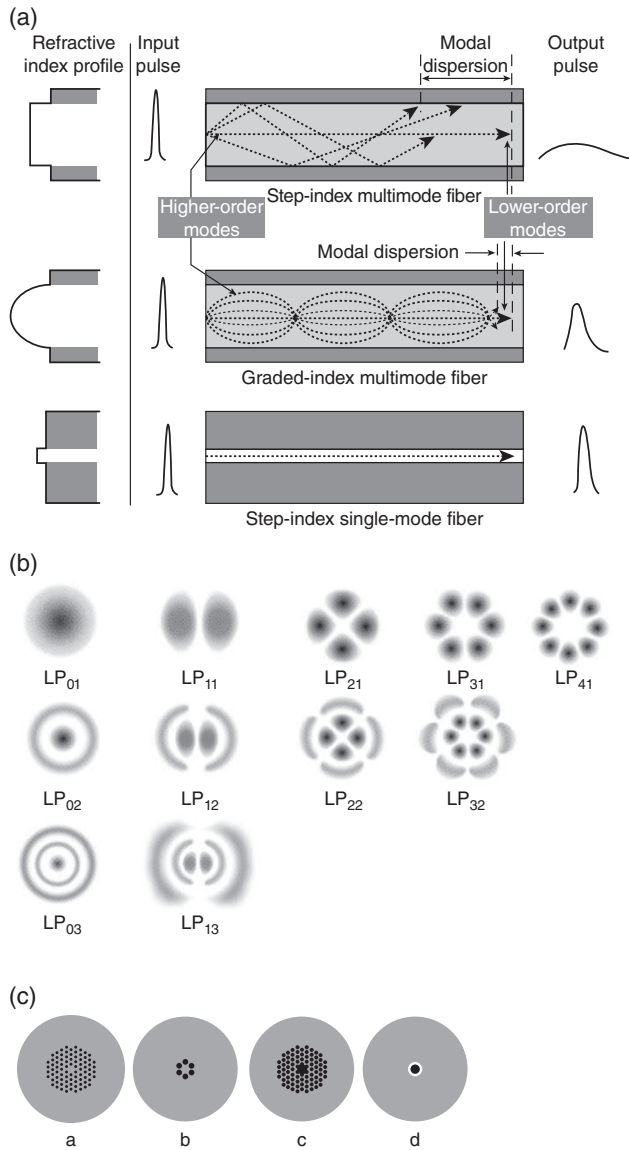


Figure 4 (a) Total internal reflection, single/multi- and GI fiber designs, (b) electromagnetic modes, and (c) schematic designs of photonic crystal fiber and MOF. Source: Reprinted with permission from [5].

of 62.5 μm). The fibers are doubly coated with protective polymers to resist abrasion and reduce the effects of bending such that the total fiber diameter is about 250 μm . A series of images exemplifying current standard and specialty optical fibers are provided in Figure 4.

2.2.1 Conventional Core–Clad Optical Fibers

As noted above, in the ray-optic view, optical fibers guide light via total internal reflection whereby the light is confined in the high-index core, which is surrounded by a

lower-refractive index cladding. Under this condition, i.e. light incident from a high-index region into a lower-index region, Snell's law for light refraction is violated when the angle of incidence exceeds a critical angle (given by $\sin^{-1}(n_{\text{clad}}/n_{\text{core}})$, where n_{clad} is the refractive index of the clad and n_{core} is the refractive index of the core, and reflection, instead of refraction, occurs (Figure 4a). The index difference between core and clad need not be large and actually is one of the design parameters that define the behavior of the resultant waveguide.

For simple descriptions, the ray-optic picture generally suffices. For more sophisticated designs, however, light is more correctly described as a wave, and the aforementioned ray-optic construction is replaced with a wave-optic formalism in which electromagnetic modes are confined and allowed to propagate within a higher refractive index core coaxially surrounded by a lower-refractive index cladding. In the wave-optic perspective, the transverse components of the light waves constructively and destructively interfere across the core, influenced by the cladding, yielding stable propagating fiber modes. Some of the light power inevitably extends into the cladding: this component is called the evanescent field. The exact distribution of these modes depends on the core size, refractive index contrast between core and clad (defined by the numerical aperture, $\text{NA} = [n_{\text{core}}^2 - n_{\text{clad}}^2]^{1/2}$), the wavelength of light, and the cross-sectional geometry of the core; i.e. whether rectangular, circular, elliptical, etc. Thorough reviews of conventional core/clad optical fiber designs are given in [5, 11].

One important practical consequence of the coexistence of modes in an optical fiber is modal dispersion. In communication systems, the optical fibers carry a digital (on/off) series of packets of light. Because each mode has a different distribution, it has a different effective (mode) index, hence velocity. As a result, data packets launched into a fiber that excite multiple modes will necessarily spread in time, analogously to the chromatic dispersion of pulses noted above, such that data can be lost over time/distance. Such multimode (MM) optical fibers are not only easier to fabricate and maybe better for short distance/lower bandwidth applications where ease of handling and cost are drivers. Single-mode (SM) optical fibers generally possess a smaller core and lower numerical aperture (NA) than do MM fibers such that only the lowest-order mode propagates and no modal dispersion is present. Single-mode fibers are required for high-capacity communications over longer distances. Graded-index (GI) fibers are MM waveguides where the refractive index across the core is graded in a nearly parabolic manner, which balances the time for a given mode to propagate a certain direction. As a result, modal dispersion is significantly reduced [5, 11].

2.2.2 Double-Clad Optical Fiber

Optical fibers whose core has been doped with light-emissive species can be used as an optical amplifier or laser. The details and uses of these fibers are provided in Sections 2.1.2 (Active Optical Properties) and 5 (Applications), respectively, and so will not be described at length here. Suffice it to say that the excitation of the active species requires an optical pump; efficiently collecting the pump light into the fiber core can be problematic given the core's often small size. One approach to lessen this difficulty is to pump the larger cladding, rather than the core directly. In order to do this effectively, the cladding must itself act as a waveguide: a secondary cladding of lower-refractive index surrounding the higher refractive index active core is then necessary. This "double-clad" design is particularly useful in high-power (>1 kW) fiber-based laser designs where significant pump powers are required to achieve the desired laser output power. Additionally, double-clad fibers permit the use of lower-brightness diode sources for efficient pumping of the active core through brightness conversion of light in the cladding. The cross section of this pump cladding often is shaped, such as with a flat edge or hexagonal symmetry, in order to break the circular symmetry and facilitate intersection of the helical cladding modes of the pump with the active core. This design provides a means both of efficient pumping and excitation. References [9] and [5] provide excellent additional details on double-clad designs and uses.

2.2.3 Microstructured and Photonic Crystal Optical Fiber

MOFs and photonic crystal fibers (PCFs) constitute classes of optical fibers where the cross-sectional geometry is periodically modified in order to control the propagation characteristics of the light [12]. These periodicities in the material, whose length scales generally are commensurate with the wavelength of light, beget periodicities in the refractive index profile that create Bragg-like conditions for allowed and forbidden propagation energies and directions associated with the transverse components of the electromagnetic modes. For completeness, it is noted that some dispersion shifted/flattened (telecommunications) fibers have index structures that can be several times larger than the wavelength. A representative image of a PCF cross section is provided in Figure 4. Though MOFs and PCFs have been fabricated from a wide variety of glasses, the majority of structures are based on silica given its high strength, low loss, and commercial availability. The ability to use both silica and the fiber's geometric structure to realize properties that a conventional silica fiber would not otherwise possess has opened many doors to important applications, such as sensing, low-latency communications, and supercontinuum (SC) generation. As the

creation of a continuous and broad spectra, SC generation arises when short, high-power laser pulses propagate through a nonlinear media (here the fiber). Such spectral broadening can rely on a variety of nonlinear effects, including SPM, FWM, soliton fission, and Raman scattering. While SC generation can be observed in many nonlinear media, MOFs and PCFs are particularly useful because they can provide for small mode sizes and tailored dispersions that facilitate enhanced nonlinearities [13].

3 Optical Fiber Glasses

3.1 Silica and Silicates

As specifically relates to optical fiber, silica has always been the main glass former used in all practical and large commercial scales. This is due to the purity and vapor-phase processability of the precursor SiCl_4 . Both as a glass and as an optical fiber, SiO_2 can be produced with nearly intrinsic properties, of which the most important are transparency and strength.

Within the spectral region of low intrinsic loss, silica exhibits a minimum transmission of about 0.2 dB/km at a wavelength of 1.55 μm . The V-curve for silica was provided in Figure 2. Silica glass is the only material for which the theoretical transmission and that measured in practice coincide, again a testimony of testament to the degree of engineering and optimization of the CVD processes employed in the manufacturing of silica optical fiber. For all intents and purposes, impurities have been removed from the process, though, in some cases, such as for non-commodity (i.e. specialty) designs and compositions, some impurities can still be present. Near the low-loss wavelengths in silica, transition metals, rare earths, and hydroxyl groups (OH) can limit transparency. It is worth noting that high OH concentrations in SiO_2 glass do improve its ultraviolet (UV) transmission, so that optical fibers for application in the UV spectral range do typically have OH purposely included.

When properly drawn and coated, silica-glass optical fibers can also exhibit nearly theoretical tensile fracture strength, in excess of 3 GPa. This is due in part to the high draw temperature, which can anneal away any cracks or scratches on the glass surface. The high strength of SiO_2 glass correlates with its refractory thermal nature (both originating from the strength of the Si–O bond) and its relatively high chemical inertness and high laser damage threshold. Not surprisingly, the centrality of silica glass to all optical fiber applications of commercial consequence stems from this remarkable combination of properties; see Table 1.

A variety of oxides generally are added to silica to modify its refractive index, thermal expansion coefficients, and viscosity as a function of temperature. The most

Table 1 Representative properties for common optical fiber glasses.

	n^a	$n_2/n\text{SiO}_2^b$	Transparency range ^c	T_g (°C)	CTE ($10^{-6}/\text{K}$)	Principal applications
SiO ₂	1.44	1	0.3–2.1	1120	0.55	Communications, fiber lasers
ZBLAN	1.49	1.2	0.5–5.5	265	17.2	IR fiber lasers and light transport
Phosphate ^d	1.55	1.2	0.4–2	360	95	High gain per unit length fiber lasers
Germanate ^d	1.8	40	0.5–4	450	100	Nonlinear fiber optics
Tellurite ^d	2	20	0.5–4.5	300	170	Nonlinear fiber optics
As ₂ S ₃	2.5	200	6 Jan	180	21	Nonlinear and IR fiber optics
As ₂ Se ₃	2.9	600	1.5–9	140	24	Nonlinear and IR fiber optics

^a Refractive index at a wavelength of 1550 nm.^b Nonlinear refractive index at a wavelength of 1550 nm relative to that of SiO₂.^c Transparency range of glass in fiber form.^d Representative order of magnitude values for these selected glass families.

Source: After [14].

common are GeO₂ (germanosilicates), Al₂O₃ (aluminosilicates), P₂O₅ (phosphosilicates), F (fluorinated silicates), and B₂O₃ (borosilicates). When added to SiO₂, GeO₂ increases the refractive index and enhances photosensitivity, P₂O₅ increases the refractive index and reduces glass viscosity, Al₂O₃ increases the refractive index and enhances the solubility of rare earth dopants, B₂O₃ reduces the refractive index and increases the coefficient of thermal expansion, and F reduces the refractive index and the glass viscosity.

Doping with laser-active species, most notably the rare earths, is employed for the realization of optical-fiber amplifiers and lasers. In the case of active optical fibers based on silica, a dopant is often required to lessen phase separation of the glass and the resulting clustering of the rare earth oxide (RE₂O₃) since the RE₂O₃–SiO₂ systems display considerable immiscibilities [15]. Alumina (Al₂O₃) is the most common additive to silica though phosphorus pentoxide (P₂O₅) also can be used. Greater detail on silica and silicate-based optical fibers can be found in [11, 15] as well as in references therein.

3.2 Phosphates

Phosphates constitute a family of oxide glasses where the principal glass-forming species is phosphorus pentoxide, P₂O₅ (Chapter 7.9). The structure of phosphate glasses is based on PO₄²⁻ tetrahedra whose P=O double bond is credited for the reduced thermal and mechanical properties of phosphate glasses in comparison with silicates. Although P₂O₅ is considered a glass former, phosphate glasses are always multicomponent with a wide range of possible network intermediates and modifiers. Of particular note are the alkaline earth oxides (i.e. MgO, CaO, SrO, and BaO), alkali oxides (i.e. Li₂O, Na₂O, K₂O), and sesquioxides (e.g. Al₂O₃ and B₂O₃). Each contributes in

different ways to increase chemical durability and decrease the phosphate glass solubility in water and tendency to devitrify. Given the broad range of phosphate glass compositions, it is difficult to define specific draw temperatures or optical and thermal property values. Suffice it to say that phosphates are considered soft glasses; they definitely have reduced mechanical strength relative to silica and typically draw into fiber at temperatures of the order of 800°C. Attenuation values from fibers reported in the literature range from about 0.1 to several dB/m in the near IR spectral range; see Table 1.

Phosphate glass optical fibers are used most notably for fiber lasers and amplifiers with high gain per unit length. As already noted, the impact of optical nonlinearities scale with distance and so shorter amplifiers and lasers imply a reduced buildup of parasitic effects as well as reduced device dimensions. Phosphates can incorporate a higher rare earth concentration prior to the onset of concentration quenching than can conventional silicate glasses. Phosphates can, for instance, accommodate rare earth (e.g. Yb³⁺) doping concentrations higher than silica by about one order of magnitude.

3.3 Infrared Glasses

3.3.1 General Remarks

Infrared glasses are generally defined as transmitting light at wavelengths beyond the transparency range of conventional silica-based glasses and fibers. This includes the mid-infrared spectral region, from about 2–5 μm wavelengths, and the far infrared, which ranges from about 8–12 μm wavelengths and possibly longer. Interest in these spectral regions stems from the fact that these are associated with the sensing of biological and chemical species (~ 3 –12 μm range), thermal signature identification and countermeasures (~ 8 –12 μm range),

astronomy/cosmology ($\sim 8\text{--}12\ \mu\text{m}$ range), and weather forecasting ($\sim 3\text{--}5$ and $8\text{--}12\ \mu\text{m}$ range).

In general, infrared glasses are characterized by constituents that are heavier in molar weight and/or weaker in bond strength than conventional silicates. The combination of heavier structural species and weaker bonds serves to shift to longer wavelengths the multiphonon vibrational absorption bands. Since the region of lowest intrinsic loss for a glass is near the wavelength where the edge of these absorption band intersects the attenuation associated with Rayleigh scattering, this redshift in the molecular absorption band yields an intrinsically lower-loss optical fiber. Lower-loss optical fibers are of great interest for long-haul communications and high-energy lasers. Additionally, the reduced vibrational energy also implies a lower non-radiative (multiphonon) relaxation rate for active light-emissive dopants in these glasses. As a result, light emission from infrared glasses is intrinsically more efficient than in higher phonon energy silicates.

A thorough treatise on infrared optical fibers, the glasses from which they are made, how they are fabricated, their properties and applications is given in [14] and in Chapter 6.5. Accordingly, only a brief description of these important glass families is provided here. Table 1 provides a comparison of properties for selected oxide and non-oxide infrared glasses.

3.3.2 Heavy Metal Oxides

Heavy metal oxide (HMO) glasses fill a somewhat unique niche in optical-fiber glasses because they are *oxides*, thus exhibiting some of the beneficial properties of silicates, such as relatively high strength and thermal stability while being composed of heavier species and so possessing extended transparency into the infrared. The two systems most commonly studied and fabricated into optical fibers are the tellurites and germanates.

Tellurite glasses are based on TeO_2 . They were first studied in 1952 and then considered for optical fiber only in 1994. Relative to silica and to other infrared glasses, tellurites enjoy a wide transmission window that extends from the UV to the mid-IR ($\sim 0.35\text{--}5\ \mu\text{m}$) and have glass and chemical stability appropriate for many applications, high linear and nonlinear refractive indices, and relatively low phonon energy ($\sim 600\text{--}800\ \text{cm}^{-1}$ for tellurites versus $1100\ \text{cm}^{-1}$ for SiO_2). They are, however, less thermally stable with glass transition temperatures of only about $300\text{--}350\ ^\circ\text{C}$.

For optical fibers, the best-studied tellurites are related to the $\text{TeO}_2\text{--ZnO--Na}_2\text{O}$ system, common dopants further including La_2O_3 and WO_3 . Tellurites, which generally are made via a melt/quench method, often possess hydroxyl (OH) impurities that limit transparency unless dehydration methods are employed not only for their precursors but also during the melting process. The lowest

tellurite fiber attenuation values achieved to date are about $0.5\ \text{dB/m}$ at a wavelength of $2.1\ \mu\text{m}$ [14].

Another important HMO glass family is germanate glasses whose structures are analogous to those of silicates because GeO_2 is isostructural with SiO_2 . Since GeO_2 is heavier than SiO_2 , however, germanates transmit further into the infrared and have similar intrinsic losses as SiO_2 (though IR absorption is redshifted, Rayleigh scattering would be higher due to the higher refractive index) but are less thermally stable than silica. The glass transition temperature and melting point for GeO_2 are about $700\ ^\circ\text{C}$ and $1115\ ^\circ\text{C}$, respectively, whereas for SiO_2 these values are ~ 1400 and $1726\ ^\circ\text{C}$.

Germanate glasses often are multicomponent. They are typically realized through a melt/quench process. Even though GeO_2 regularly is doped into silica with one of the CVD processes, the direct formation of GeO_2 core optical fibers is made difficult by significant mismatches in thermal expansion. That said, silica-clad optical fibers possessing very high GeO_2 core concentrations and losses of only about $20\ \text{dB/km}$ at $1.9\ \mu\text{m}$ have been realized [16].

Of the main oxides used for optical fiber (SiO_2 , GeO_2 , P_2O_5 , and B_2O_3), GeO_2 has the highest (linear) refractive index, nonlinear refractive index (n_2), peak Raman scattering cross section, and photorefractive effect. The large n_2 value, approximately three times higher than in SiO_2 , suggests germanate glass optical fibers for four-wave frequency conversion devices. The high Raman gain of GeO_2 , approximately 10 times larger than for SiO_2 , marks these glasses as useful for efficient fiber-based tunable Raman fiber lasers and amplifiers. Lastly, the strong photosensitivity of GeO_2 , both when doped into SiO_2 and as a germanate glass, suggests the ability to write Bragg gratings into the fiber at lower UV fluence levels and without hydrogen loading as is often done for silica fibers.

Some useful compositional, physical, and optical properties of the more common tellurite and germanate glass optical fibers are provided in [14].

3.3.3 Fluorides

Fluoride glasses were discovered accidentally in the early 1970s through attempts to grow fluoride laser crystals. The ionicity of the fluoride bond makes fluorides nontraditional glass-forming systems relative to oxides and chalcogenides (Chapter 6.5). The melts generally exhibit low viscosities, and glass formation largely is based on the “confusion principle” whereby the presence of multiple components make it difficult for a crystal to form upon cooling of the melt. Relative to other infrared glasses, fluorides generally exhibit the lowest refractive index and optical nonlinearity, which makes them of value for high-power laser applications.

The first fluoride glasses were based on ZrF_4 as the main constituent. To date, the most common and

well-studied fluoride glass is “ZBLAN” (Chapter 6.5) whose base molar composition is about $53 \text{ ZrF}_4 - 20 \text{ BaF}_2 - 4 \text{ LaF}_3 - 3 \text{ AlF}_3 - 20 \text{ NaF}$. In addition to the fluorozirconate glasses, others of interest include fluoroaluminate glasses, based on aluminum fluoride, and fluorindate glasses, based on indium fluoride. The fluoroaluminates and fluorindates generally possess better chemical stability than do fluorozirconates. Mixed anion systems, such as the fluorophosphate and oxyfluoride glasses, have also been developed.

As noted, relative to silicates, infrared glasses generally possess weaker bonding, which also means reduced thermal and mechanical properties. For example, the glass transition and fiber draw temperatures for ZBLAN optical fiber are about 260 and 310 °C, respectively, whereas recent strength values of 700 MPa for 125- μm fibers have been realized. For telecommunication-grade silica optical fiber, these values are about 1100 °C (T_g), 2000 °C (T_{draw}), and > 3 GPa.

The weak bonding is useful for intrinsically low-loss and higher-efficiency lasing; however extrinsic factors have always plagued the transmission of fluoride optical fibers. In theory, ZBLAN should exhibit a minimum loss of $\sim 0.01 \text{ dB/km}$ at a wavelength of 2.5 μm , which is approximately 20 times lower than that of silica (0.2 dB/km at 1.5 μm). Whereas the record low loss to date is $\sim 0.4 \text{ dB/km}$ at 2.35 μm , typical background loss of commercial fluoride fibers is $\sim 150 \text{ dB/km}$ for ZrF_4 -based glass fibers (wavelength range of 2.3–3.6 μm) and $\leq 450 \text{ dB/km}$ for InF_3 -based glass fibers (wavelength range of 3.2–4.6 μm). Only silica-based glasses are reliably manufactured with the CVD process; all other glasses being made by a melt/quench method, which leads to added impurities. In the case of the fluorides, these higher losses are associated with transition metal, rare earth, and OH impurities as well as extrinsic scattering from occasional bubbles, crystallites, and inclusions.

That said, even with present loss values, the reduced phonon energies (600 cm^{-1} for ZBLAN versus 1100 cm^{-1} for silica) associated with the weak bonding have permitted a wide range of novel fluoride glass fiber lasers at wavelengths not possible with silicates. Of particular note are numerous fluoride glass fiber lasers doped with rare earths based on upconversion of near-infrared pumps to visible and UV wavelengths [7] and also the praseodymium-doped fluoride fiber that amplifies communication signals at the 1.3 μm zero dispersion wavelength.

For completeness it is worth noting that fluorides are part of the broader halide family of non-oxide glasses (Chapter 6.5). Generally speaking, fluorides are more stable and possess a greater glass-forming range than do glasses based on other halide glass formers such as ZnCl_2 .

3.3.4 Chalcogenides

Chalcogenide glasses derive their name from the chalcogen elements from which they are formed, namely, sulfur (S), selenium (Se), and tellurium (Te); see Chapter 6.5. The glass-forming ability of this glass family tends to decrease with increasing molecular weight; i.e. it decreases in the order sulfides, selenides, and tellurides (which are based on elemental Te and thus not to be confused with the TeO_2 -based tellurites already described). The best-studied and commonly employed systems are in the binary systems of As with S, Se, and Ge and in the ternary systems of As–Se with Ge and Te, as well as in the Ge–As–Te, Ge–Sb–Se, and Ga–La–S families. The glass transition and fiber-draw temperatures range from 350 to 550 °C and from 400 to 700 °C, respectively.

From the perspective of optical fiber, chalcogenides are of greatest interest for mid- and long-wave IR light propagation. The relative heaviness of the constituent elements coupled with weaker bond strengths shifts the infrared absorption out to quite long wavelengths, in some cases in excess of 20 μm . This makes such fibers of value for astronomical observations and imaging where no other glasses or fibers transmit. In addition to this extended transparency in the infrared, chalcogenides have the highest nonlinear refractive indices (n_2) among optical glasses, making them of interest for low-power fibers in nonlinear optical devices.

The minimum intrinsic loss of chalcogenide optical fiber is near or slightly below that of silica, though at longer wavelengths, e.g. $\sim 0.01 \text{ dB/m}$ at 5.0 μm for As_2S_3 . In practice, however, losses generally are considerably higher because of impurities from the melting process as well as glass and homopolar bond defects. More typical mid-infrared attenuation values are in the range of 0.1–10 dB/m. To date, the lowest loss observed in a chalcogenide is 0.012 dB/m at 3.0 μm from a multimode As_2S_3 optical fiber.

4 Optical Fiber Fabrication

The fabrication of optical fiber requires specific materials possessing the requisite optical, physical, chemical, and thermal properties for a given fiber design, which can, in addition, be converted from either the melt or a glass “preform” or “blank” into the resultant fiber. This section describes the basics of these two considerations.

4.1 Glass Formation

There are many ways in which to make a glass. For the purposes of this Chapter, only those that are used in

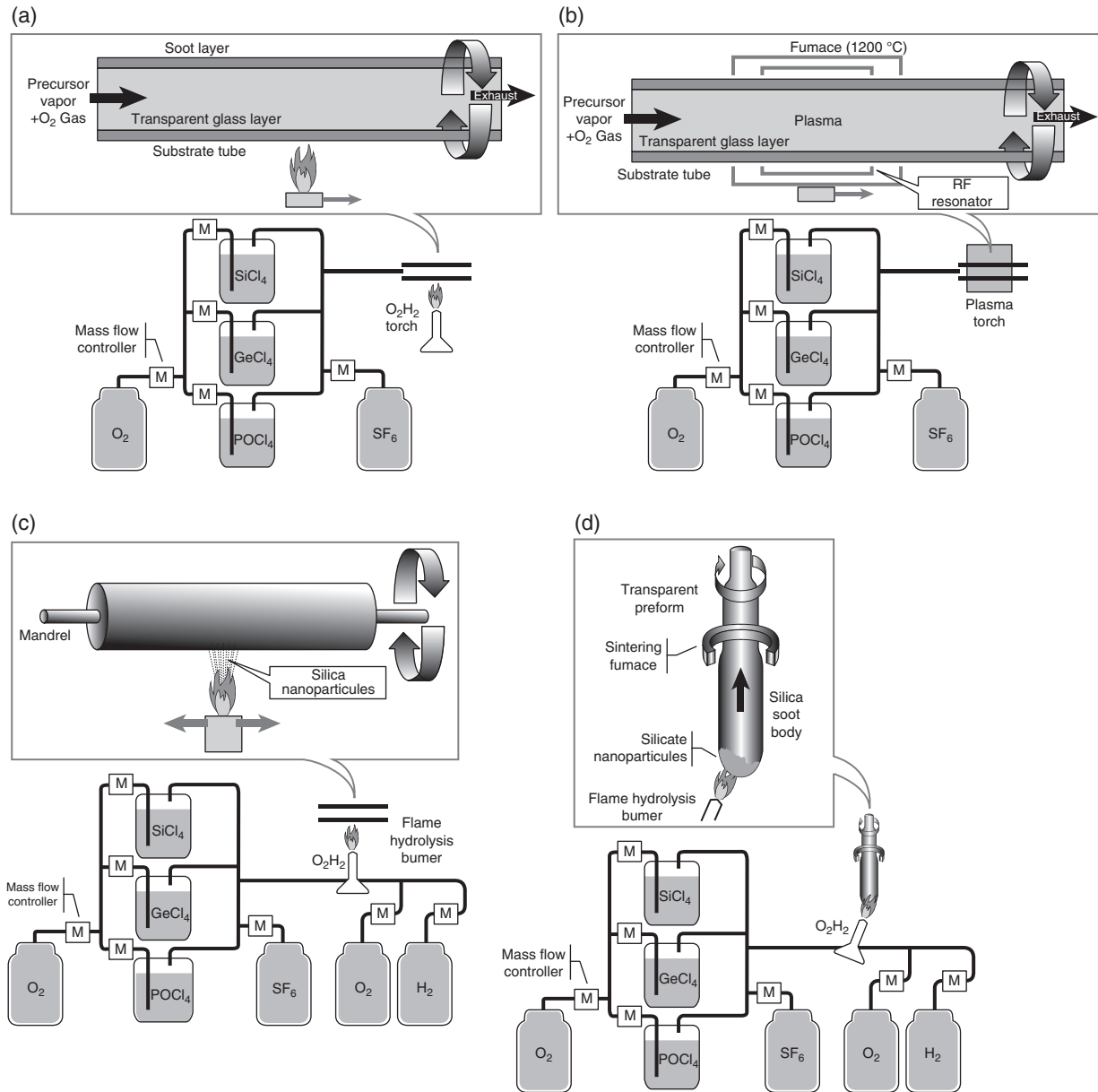


Figure 5 Sketch of the chemical vapor deposition process (a) modified chemical vapor deposition (MCVD), (b) plasma-enhanced chemical vapor deposition (PECVD), (c) outside vapor deposition (OVD), and (d) vapor axial deposition (VAD). Source: After [5].

reasonable scale to make glasses relevant to optical fiber are noted. Thorough reviews of conventional optical fiber fabrication are given in [11] and [5] and of photonic crystal fibers are given in [5]. Representative schematics for the CVD processes as well as the fiber-draw approach to fiber formation are provided in Figures 5 and 6.

4.1.1 Melt/Quench

Rods and tubes can be extracted from melt-quenched glass, typically via milling and polishing, from which a

core/clad preform can itself be constructed based on the optical fiber design. Judicious selection of the starting materials that are batched and melted in an appropriate crucible is critical to obtaining the requisite refractive index, thermal expansion coefficient, and viscosity–temperature relationships, among other important properties. Depending on the chemistry of the melt, and particularly on the vapor pressure of its constituents, additional conditions may be necessary such as a controlled, low-oxygen content atmosphere as in the case of fluoride glasses or sealed ampoules for the melting

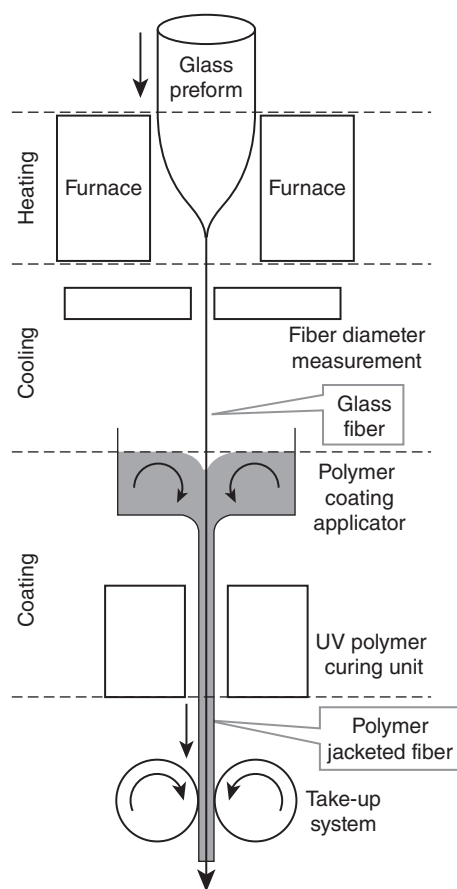


Figure 6 Sketch of the fiber-draw process. *Source:* After [5].

of high-quality and high-purity chalcogenide glasses. Contamination caused by dissolution of the crucible into the glass melt and by impurities resident in the precursor batch compounds can yield extrinsic absorptions and modify the physical and chemical properties that limit the performance of the subsequent glass. Additionally, contamination of the glass from atmospheric moisture can be problematic since OH species strongly absorb at many wavelengths of practical interest. Care must be given in all instances to make the melt, hence resultant glass, as free of impurities, bubbles, and chemical heterogeneities as possible for optimal fiber formation and optical performance.

4.1.2 Chemical Vapor Deposition

All silica-based optical fiber of commercial consequence is drawn from glass fabricated using chemical vapor deposition methods, namely, outside vapor deposition (OVD), modified chemical vapor deposition (MCVD), vapor axial deposition (VAD), or plasma-enhanced chemical vapor deposition (PECVD). Representative schematics are provided in Figure 5 for these processes

whose applications to the fabrication of optical fiber is thoroughly described in [5, 11].

In all cases, the base reaction is $\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2$. Though the processing specifics differ, the enabling chemistry is similar; i.e. the high temperature oxidation, thermophoretic deposition of glass particulate soot, and subsequent sintering and consolidation of glass soot derived from volatile halide species. The exact temperatures and times required for each of these steps differ, depending on the processing method, the size and design of the preform, and the compositions of the glasses.

In addition to yielding a final glass rod that contains both core and clad region in their desired proportions, the particular power of these CVD approaches is that SiCl_4 possesses a vapor pressure that is nearly 10^{12} times higher than those of the most detrimental impurities to optical performance, transition metals phases such as Fe_2Cl_6 . Hence, CVD-derived silica-based optical fibers can exhibit intrinsically low attenuation values.

In order to obtain silicate optical fibers, the GeO_2 , P_2O_5 , B_2O_3 , and/or F additives to the SiO_2 are formed through vapor-phase reactions from their respective volatile halides: GeCl_4 , POCl_3 , BCl_3 , and/or SiF_4 . Either because BCl_3 (or BBr_3) and SiF_4 are gases or because the GeCl_4 and POCl_3 precursor liquids have a suitably high vapor pressures, in both cases the doping chemical can be added directly into the SiCl_4 gas stream. As done for doping with Al_2O_3 or light-emissive rare earth species [5, 11], one can adjust further the glass composition by doping the deposited soot via solutions with dissolved salts (e.g. AlCl_3 , YbCl_3 , and ErCl_3). A complete solid solution exists between SiO_2 and GeO_2 and P_2O_5 such that glass stability is not problematic, though some volatility of the GeO_2 and P_2O_5 can occur at the high temperatures required for preform consolidation and collapse. This volatility can lead to undesirable changes in the refractive index profile of the resultant preform, which in turn influences the performance of the resultant optical fiber. Other dopants, such as Al_2O_3 , B_2O_3 , and the lanthanide oxides (e.g. Yb_2O_3), do possess compositional regions of liquid-liquid immiscibility or a tendency to crystallize. Accordingly, more limited ranges exist for their addition into SiO_2 though novel methods for obviating these traditional issues have been developed [15].

4.2 Fiber Formation

As with glass formation, there are many ways to make a fiber. Whereas many polymer fibers, and indeed some non-optical glass fibers, are fabricated by extrusion, optical fibers are not because of the critical need for a pristine surface from which the strength of the resultant fiber is largely determined (see Chapter 3.12). Glass optical fibers are either formed directly from the melt in some specialty

cases or, more conventionally, drawn from a (core/clad) glass rod directly into fiber. These processes are described in more detail below.

4.2.1 Double Crucible

Glasses such as selected chalcogenides are not sufficiently stable to yield a bulk rod. They can be formed into fibers instead by melting of the components followed by controlled flow of this melt out of an orifice at the bottom of the melter. In order to achieve a core/clad geometry, one melt stream (generally that of the core) is initiated, and a second melt stream (generally that of the cladding) is then flowed around it; these melt streams originated from concentric melters, each controlled to melt uniformly, homogenize the core or clad glass, and yield a stream with proper melt viscosity such that limited interactions between core and clad result upon fiber formation.

4.2.2 Fiber Draw

The draw process is vastly dominant to fabricate optical fibers. It is distinct from extrusion, spinning, or pultrusion in that a nozzle or die is not employed. These processes are applicable to polymer fibers (optical and non-optical) as well as non-optical glass fibers such as those used for thermal insulation or acoustic isolation (Chapter 9.3). Because fiber strength is of paramount importance, particularly in telecommunication applications, the surface of the (typically silica) optical fiber cannot be contacted, obviating the use of a die or spinneret through which the fiber is formed.

Whereas the fiber is formed directly from the melt in the double-crucible method, the fiber-draw process begins with a glass rod (also called a preform or blank) that contains the core and clad glasses. The subsequent reduction from preform to fiber generally is an affine transformation whereby the diametric ratio of core and clad remains constant. If pressure or vacuum is employed during the draw, as is occasionally done in the fabrication of photonic crystal fibers, then the geometric ratios between preform and resultant fiber are not necessarily constant, and pressure is another processing parameter in the ultimate fiber design and performance.

In general, glass optical fibers are formed with a vertical draw tower. The glass preform is held at the top of the tower in a down-feed unit that controllably lowers it into a furnace. Under certain circumstances, the preform can be rotated during the draw to facilitate greater uniformity of cross-sectional core diameter or to induce helical perturbations along the fiber's length. The furnace design, often including inert atmosphere control, depends on the glass from which the fiber is made. The temperature of the furnace usually is best determined from the tension of the fiber during the draw, which is important for

maintaining good diameter control: a temperature appropriate in this respect is typically that at which the viscosity is about 10^6 poise (10^5 Pa·s). For conventional silica optical fibers, these temperatures are between about 1925 and 2000 °C. For softer glasses that are either prone to crystallization or have steeper viscosity–temperature relationships, the working range can be markedly shorter ($\Delta T \sim 10\text{--}20$ K).

During the beginning of the fiber-draw process, the temperature usually is raised above the eventual draw temperature in order to hasten the softening of the glass preform and its localized flow into a “drop” or “gob” that ultimately exits the furnace and defines the transition from bulk preform into fiber. This transition section is also known as the “neck” or “neck-down” region. The fiber is then pulled down the tower through a series of other instruments such as those that measure the bare (core/clad) glass fiber diameter, apply and cure polymer coatings (more detail below), display the concentricity of the coating around the glass fiber, measure the final coated fiber diameter, provide the tension for pulling the fiber from the locally softened preform (which is slowly lowered into the furnace), and ultimately collect the fiber on a spool for subsequent use.

Upon sufficient cooling of the fiber, though still on-line prior to collection, one or often two polymer coatings are applied. In most cases, they provide protection of the underlying glass from the strains and abrasions of installation and use (Chapter 3.12). The first polymer layer, called the primary coating, is relatively soft and is intended to relieve the strain placed on the fiber during use so that the loss of light caused by micro-bending can be lessened. The second polymer layer, called the secondary coating, is generally hard and provides abrasion resistance. The coatings are applied in oligomeric form to the glass fiber on-line during the draw by a series of dies that do not contact the glass surface but do provide a thin separation for the coating to wet the glass with well-defined thickness. The coatings are then cured on-line with an ultraviolet lamp. Whether the primary is cured first or both primary and secondary coatings are cured simultaneously (called wet-on-wet coating) depends on the application, hence volume of fiber and draw speed. For more specialty uses, a single coating may be sufficient. One variation on this theme includes polymer clad silica (PCS) where the fiber is only composed of silica with no core/clad structure and the single (hard) polymer coating constitutes the cladding. A second variation is double-clad fibers used in fiber laser designs, where the fiber is constructed with an active glass core, passive glass clad, and a low-refractive index polymer cladding that provides light guidance for the laser pump light in the glass cladding. A protective outer polymer coating often is used in double-clad fiber designs.

For completeness, the aforementioned microstructured and photonic crystal optical fibers generally are formed via fiber-draw processes as well. However, the preforms from which the fibers are drawn typically are ensembles of stacked rods or tubes of requisite periodic structure. Although tedious, this “stack and draw” method does enable very sophisticated and multi-material structures to be fabricated and drawn into fiber.

5 Applications

In 2013, the National Research Council of the United States National Academies published an updated report on the state of optics and photonics [17] whose annual global economic impact was estimated at \$7.5 trillion. Optical fiber is a subset of this field, which was fully expected to continue to grow because of their many direct or indirect applications. The principal application areas are (i) communications, information processing, and data storage; (ii) defense and national security; (iii) energy; (iv) health and medicine; and (v) advanced manufacturing. It is beyond the scope of this chapter to delve deeply into each though a brief description is provided below. For more detail, the reader is referred to the report itself [17].

Much of the initial impetus behind the development of optical fibers stemmed from their potential use in communications. It can be argued that of all the applications of glass optical fibers, those for global communications remain not only the largest in scale but also the most enabling since such fibers have brought knowledge and given voice to people around the world who previously had no access to information or means for commerce. Around the turn of the twenty-first century, a meaningful transition occurred when Internet traffic associated with data surpassed that for voice-based telephony. People speaking with people approximately scales with population, which grows at a rate of only about 1% per year. Computers talking to computers do not, so very rapid increases in Internet traffic spurred a growth in the demand for glass optical fiber that continues to this day. The Internet of Things, continued growth in social media, cloud computing, and data storage will only increase this demand in the future.

There have always been defense and security applications for optical fiber, and indeed, the Internet evolved from the US Department of Defense’s Advanced Research Projects Agency Network (ARPANet). The dielectric nature of glass obviates many electronic means of tapping into signals, making optical communications more secure. More recently, the use of lasers for projecting nearly instantaneous power at long distances without having to risk harm to individuals has ushered in

significant growth in high-energy lasers. Though free-electron, chemical, and solid-state lasers are all of interest, high-energy lasers based on glass optical fibers have enjoyed considerable attention because they can be small, light, fully integrated, and meet many of the requisite power needs [9].

The main use at present of optical fiber as relates to energy is for the monitoring of oil and gas wells. In particular, glass optical fibers are employed in distributed temperature and acoustic sensor systems, which can allow for increased production and reduced risks. The high pressures, temperatures, and chemically aggressive environments have all but limited the choice of optical fibers to those made from either silica or, in some cases, pure silica cores with lower-index fluorinated silica cladding, which resist hydrogen degradation better than other glass families. There have been recent successes in using high-power lasers for actual drilling, which could greatly speed the exploration of new wells.

Photonics plays an ever expanding role in health and medicine where the intrinsically small dimensions and flexibility of glass fibers are most valuable advantages. Applications include fiber bundle endoscopes for imaging within the body, fibers as light pipes to induce localized chemical reactions associated with photodynamic therapies, and more recently, though yet immature, optogenetics whose goal is to control and record neuron activity in living organisms. Infrared optical fibers – particularly fluoride glass optical fibers – are used to transmit mid-infrared light such as that at 2.8 μm from an Er : YAG laser for use in ophthalmology and dentistry.

Advanced manufacturing has grown markedly over the past decade as modern conveniences continue to shrink in dimensions and increasingly complicated shapes are more rapidly fabricated. While lasers in general play enabling roles, the specific use of glass optical fiber is more limited but growing as with some of the other applications noted above. The use of fiber in advanced manufacturing, at present, largely relates to its flexibility such that laser light can be brought from the source to the part being fabricated without complex bulk optical elements where misalignment can occur in articulated robotic systems. A second and growing area for glass optical fiber in manufacturing relates to fiber-based high-power lasers where the quality of the laser beam can be considerably higher than in bulk solid-state laser systems.

6 Perspectives

To say that optical fiber is central to modern life is an understatement. The ubiquity and instantaneous availability of information, as just one example, is entirely

enabled by optical fibers in both passive and active forms. While silica will remain the material of choice, continued advances in infrared glasses, most likely fluorides, will open doors to new applications [5]. Ever greater control of the properties of light will be engineered into the fibers through judicious and clever combinations of geometric structuring and materials selection [8]. In addition to expanded roles in present technologies such as communications, defense, medicine, and manufacturing, applications where fibers play more enabling roles will grow and include energy independence, advanced genomics (e.g. optogenetics), autonomous vehicles, and space exploration. Only time will tell what the future holds, but there is no question that the future for glass optical fiber remains very bright!

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6.5

Fluoride and Chalcogenide Glasses for Mid-infrared Optics

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1 Introduction

The glass world has long been dominated by oxides because of the exceptional ability of SiO_2 , B_2O_3 , and P_2O_5 to form strongly associated melts. In the last past decades, however, new glasses have been formed from metallic salts such as fluorides and chalcogenides whose unusual properties, primarily optical, have led to important practical applications. Research and development in this field has in fact been boosted by the need for light-transmitting materials in the infrared (IR) region. In contrast to oxides glasses, whose opacity beyond $3\text{ }\mu\text{m}$ make them inappropriate for mid-IR technologies, fluoride and chalcogenide glasses are low-phonon materials because the vibrational modes of their glass framework shift the IR cutoff to a maximum of about $20\text{ }\mu\text{m}$. This is why chalcogenides [1–3] and fluorides [4, 5] have found many applications, ranging from IR lenses as key components in thermal-imaging and night-vision systems to optical-waveguide fibers transmitting IR light in energy transfer or remote analytical devices.

This chapter will focus on those glasses for which applications have been found, thus excluding a number of halides (chloride, bromide, and iodine) and chalcogenides that suffer from a poor chemical durability, especially under humid conditions, or from weak mechanical properties and resistance to crystallization. The first series of materials selected encompasses complex ZrF_4 -based glasses known as ZBLAN, because they are a mix of Zr, Ba, La, Al, and Na fluorides, as well as metal trifluorides such as InF_3 , GaF_3 , or AlF_3 [5]. The second group to be discussed deals with composition ranges where viscous liquid may be formed from chalcogens ($\text{X} = \text{S}, \text{Se}, \text{Te}$). This group also

includes glasses made from chalcogenides such as As_2X_3 , Sb_2X_3 , GeX_2 , and Ga_2X_3 [1, 6, 7]. After having briefly reviewed the issue of glass transparency, we will describe vitrification in these systems, then glass structure, and finally the main current uses of these materials in optics. For detailed information on important topics directly relevant to the present theme, we will refer to other chapters on floppy–rigid structural transitions (Chapter 2.7), luminescence (Chapter 6.3), silica optical fibers (Chapter 6.4), and glass ceramization (Chapter 7.11).

2 Glass Transparency in the Infrared Region

At short wavelengths the optical transparency of a material is limited by the interaction of light with the electrons involved in chemical bonding. At high wavelengths, optical losses originate in absorption by the vibrating atoms, which form dipoles coupling with the oscillating electric field of light. As indicated by the simple model of the harmonic oscillator, the frequencies at which light begins to couple with network vibrations decrease with increasing atomic masses and decreasing bond strengths. In silicate glasses, the absorption rises to 50%, at about $3\text{ }\mu\text{m}$ in the near-IR (Figure 1). Hence, the most efficient strategy to expand the spectral window of glasses is to deal with atoms heavier than oxygen or silicon to lower phonon energy and shift the multiphonon cutoff to longer wavelengths. With fluorine, sulfur, selenium, and tellurium, the optical transparency indeed extends further and further in the mid-IR and even in the far-IR with the heaviness of the glass former (Figure 1).

In practice, the reasons for developing glasses transmitting light in the mid-IR region are several. First, blackbody emission shifts toward the IR with decreasing temperatures. Whereas the sun, with a corona temperature of

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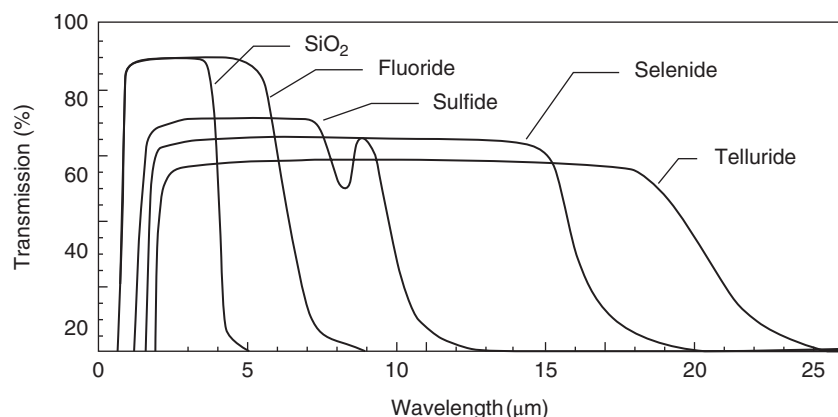


Figure 1 Influence of atomic weight and bond strength on the infrared transparency of glass families.

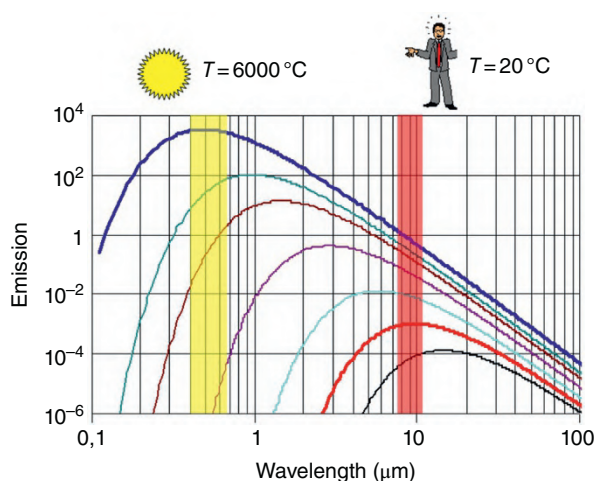


Figure 2 Shift to lower wavelengths and intensity increase with temperature of blackbody radiation. Emission by the human body in the mid-infrared near 10 μm .

about 6000 K, emits most of its energy in the visible region, the radiation emitted at room temperature – for instance, by the human body – peaks near 10 μm (Figure 2). Optics operating in this region are thus necessary for thermal imaging in night-vision systems and, more generally, for all kinds of IR camera and IR transmitting optics. Second, although generally transparent in the visible region, the atmosphere exhibits two windows where light is strongly absorbed. One is the 3–5 μm region just in between the wavelength of the O–H elongation vibration and the strong bending mode of the H_2O molecule. Extending from 8 μm , after water absorption, to about 13 μm where CO_2 molecules begin to absorb, the second window has a greater width that makes it well suited to visualize thermal objects at room temperature such as human or animal beings. Third, as already noted, the IR region is the domain of molecular vibrations. Hence, every kind of molecules has a spectral fingerprint, which is roughly located

between 2 and 12 μm , so that chemical species can be detected and analyzed from IR spectra.

For all applications, however, an important feature to be accounted for is Fresnel loss, which is caused by photon reflections at the glass surface and is proportional to the refractive index n of the material. This parameter depends on the polarization of the atoms forming the glass. It is strongly enhanced by heavy elements, so it increases from 1.5 for silicate or fluoride glasses to 2–2.5 for selenides and even to 3.2 for tellurides. As a result, reflection losses increase sympathetically from about 15 to 50%, respectively (Figure 1), which implies that the surface of chalcogenide glass lenses needs to be coated with antireflective films.

Finally, a few words are probably useful to justify why these materials cannot generally be used in the visible range. At short wavelengths (Figure 1), optical absorption is due to electronic transitions associated with both bonding and nonbonding electrons. The latter gives rise to the so-called band-gap absorption, whose cutoff wavelength is $\lambda_c = hc/E_g$ for a glass with a band gap E_g . The glass is transparent at wavelengths $\lambda > \lambda_c$ where light is not sufficiently energetic to induce an electronic transition. Conversely, the material is opaque at wavelengths $\lambda < \lambda_c$ where light is absorbed to promote an electronic transition. Because of band-gap absorption, a bulk glass thus filters out all visible light of wavelengths shorter than λ_c and can then appear colored or even black.

Oxide glasses such as silicates are transparent in the visible because λ_c is located in the UV region at around 0.3 μm . The same applies to fluoride glasses. Chalcogenides, in contrast, markedly absorb in the visible because their band gaps are lowered by the lone pairs of nonbonding electrons sitting at intermediate levels between the valence and conduction bands. Chalcogen elements, moreover, are regarded as semiconductors because they lie in between metals and nonmetals in the periodic table, so electronic transitions become increasingly probable from sulfur to tellurium. In sulfide glasses, the transmission limit is

slightly displaced in the middle of the visible range, making these materials yellow or orange. For selenides, the color becomes dark red or black, and definitely black for tellurides, making these materials looking like an alloy rather than a glass. In summary, fluoride and chalcogenide glasses are unique for mid-IR technology, but useless for the visible and near-IR ranges where silicate glasses remain matchless.

3 Fluoride Glasses: Formation and Structure

3.1 Glass Formation in Metal Fluorides MF_x

Owing to the peculiar electronegativity of fluorine, fluorides can be roughly divided in two classes [5]. When the metal M has a high oxidation state, the formation of volatile molecular species is dominant, and the chemical bond is covalent. Typical examples are uranium hexafluoride, UF_6 , and silicon tetrafluoride, SiF_4 . If the metal is mono- or divalent (e.g. alkalis or alkaline earths), the material is highly crystalline with strong ionic bonds. This is the case of NaF or CaF_2 , which upon melting give rise to fluid, nonassociated liquids lacking any glass-forming ability.

Trivalent MF_3 or tetravalent MF_4 crystals (M = transition metal belonging to the 3d or 4d series in the periodic table) form giant 3-D frameworks based on the connection of octahedra or more complex corner-sharing polyhedra. The chemical bonds causing the formation of these networks are intermediate between covalent (overlapping of orbitals) and purely ionic as typically found in AlF_6 , GaF_6 , InF_6 , ZrF_7 , or ZrF_8 . The connection between those units can be very rigid without any possibility of varying the bond angle M–F–M. In this case, the solid and melt have similar short-range structures, so crystallization is the rule upon cooling. In some very special situations, however, a fluoride melt can be made up of diverse MF_x polyhedral units mutually connected between which bond angles are floppy and, thus, vary at little energy cost for the system. This situation leads to an associated melt showing a higher viscosity. Crystal formation then is thwarted by the existence of these nonperiodic polymeric networks, which persist when the melt is cooled down. As happening for silicate glasses, the viscosity of the metal fluoride polymer increases so much when the temperature drops that a glass forms when the viscosity reaches 10^{12} Pa s.

To prevent crystallization, an empirical rule is to use complex compositions in which competition between different possibly nucleating crystals is maximum (the so-called principle of confusion). In the 1980s, the activity in the field was strongly boosted by the search for

ultra-transparent glasses at telecom wavelengths. Many fluoride glass compositions were then discovered, but only a few were found suitable for applications. Since interest mainly lies in widening the transparency window toward the IR, only heavy metal fluoride glasses such as ZrF_4 and InF_3 are relevant.

In fluorozirconate glasses, the most popular composition is that of ZBLAN glass, namely (in mol%), 52 ZrF_4 ·19 BaF_2 ·5 LaF_3 ·4 AlF_3 ·20 NaF, where ZrF_4 , AlF_3 , and LaF_3 are considered as glass formers and the large ions Ba^{2+} and Na^+ as modifiers. Glasses based on InF_3 are also of interest since they are stable enough to be drawn into optical fibers. The phonon energy is lower for InF_3 than for ZrF_4 glasses so that the former transmit better in the IR thanks to a cutoff that is slightly shifted toward longer wavelengths, at 5.5 instead of 4.6 μm for optical fibers. In practice, the composition of these glasses is also complex with molar concentration of InF_3 close to 50% and various heavy metal fluorides (BaF_2 , PbF_2 , ZnF_2 , GaF_3 , or CdF_2) to keep the phonon energy as low as possible and to prevent crystallization from happening. Besides, small amounts of alkali chlorides can be also added to adjust the refractive index.

3.2 Polymeric Networks Based on ZrF_n Polyhedra

Determining the structure of fluoride and chalcogenide glasses becomes increasingly difficult when composition becomes complex, especially when major components have themselves a complex structural role. For fluorides, the most appropriate and simplest glass for structural investigation has the ratio $ZrF_4/BaF_2 = 2$. Because this glass is very unstable, fast quenching of the melt is necessary to obtain small flakes suitable for X-ray investigations. Thanks to its rather simple composition, this $BaZr_2F_{10}$ glass has also been investigated by computer simulation. Examination of the fluorozirconate crystal chemistry is also bringing important information about ZrF_x coordination polyhedra, where x varies from 6 to 8 with a most frequent value of 7. As a matter of fact, there exist a variety of polyhedral geometries around zirconium associated with a great flexibility of the Zr–F–Zr bond angle. Since fluoride glasses were discovered accidentally in a study of atomic substitutions in crystalline $LaZrF_7$, it is of interest to note that, according to X-ray investigations [8], ZrF_7 and LaF_8 polyhedra are connected to form a 3-D network in this rare earth fluorozirconate.

More generally, structural models have been established to integrate several sources of information (Figure 3). In X-ray diffraction studies, radial distribution functions (RDF) show Zr–Zr pair correlations indicative of short and longer Zr...Zr distances compatible with

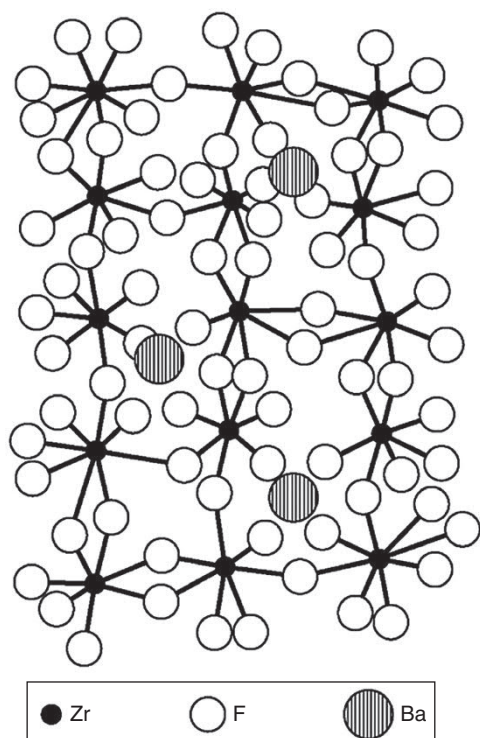


Figure 3 Structure of ZrF_4 glass reticulated by ZrF_7 or ZrF_8 polyhedral units, with large ions such as Ba^{2+} acting as network modifiers.

ZrF_x polyhedra sharing edges and corners, respectively, the Ba^{2+} ions being a glass modifier. Interestingly, computer simulations lead to the same result with two clearly distinct $\text{Zr}\dots\text{Zr}$ distances. Another important point is to establish the role played by the lanthanide atom in ZBLAN glasses. The La content being small at around 4%, Nd^{3+} has been used as a dopant because rare earth spectroscopy with this ion as a probe is very sensitive to the local ligand field. The Nd^{3+} fluorescence spectra are very similar in the glass and parent crystalline LaZrF_7 , indicating that La^{3+} is incorporated in the glass network as LaF_8 polyhedra. Hence, there is a striking contrast with silicate glasses where Nd^{3+} absorption spectra are broad, indicating that this ion is instead a network modifier.

From these results, one concludes that these associated melts vitrify when their networks have a polymeric nature. The disordered polymer is made up of a variety of polyhedral connections, including small amounts of AlF_6 and LaF_8 in addition to the predominant ZrF_7 . Variations in bond angles then cause local disorder and a lack of periodicity, whereas the Na^+ and Ba^{2+} ions are glass modifiers. Both also contribute to foster the competition between crystalline phases that might precipitate, delaying in this way the devitrification process that remains here an issue.

4 Applications of Fluoride Glasses

4.1 General Considerations

Analyses by differential scanning calorimetry (DSC) are simple means to check that glasses have the required mechanical and thermal properties and also a strong enough resistance to devitrification [5–7]. For ZBLAN, a DSC analysis shows that its T_g is close to 260°C , i.e. well above the $120\text{--}130^\circ\text{C}$ required for practical applications, but also that crystallization is signaled by an exothermic peak at T_x of about 400°C . Hence, the glass must be fiberized between these two temperatures under severely controlled viscosity conditions such that the deformation rate is high enough but crystallization remains avoided. Besides, fluoride glasses are sensitive to thermal shock because of high thermal expansion coefficients ($17.2 \times 10^{-6} \text{ K}^{-1}$ for ZBLAN), which are consistent with their rather low T_g . Heavy metal fluoride glasses are stable under normal atmospheric conditions, but they are sensitive to moisture corrosion when temperature increases because the OH^- ion has the same size as F^- , so F/OH substitution at the glass surface is a ready source of corrosion.

4.2 Optical Fibers for Guiding Infrared Light

Fibers are by far the main commercial product for fluoride glasses [4, 9], in agreement with the fact that one of the main reasons for investigating them was the search for ultra-transparent materials. Although electronic absorption in the UV is not so different in fluorides compared with SiO_2 glass, the phonon absorption in contrast drastically shifts toward long wavelengths with phonon energies of 600 and 1100 cm^{-1} , respectively. Glass transparency is represented by V-shaped curves (Figure 4), indicating that the minimum optical loss is 0.2 and about 0.02 dB/km for SiO_2 and fluoride glasses, respectively. Because fluoride glasses have thus been considered as a substitute for silica in long-distance telecommunications, much effort has been paid to develop high-quality optical waveguides in single- or multimode configurations (i.e. depending on whether the core of the fiber is several or many times larger than the light wavelength, so single or many optical modes propagate). In both cases, however, a prerequisite for the internal reflections needed for light propagation is that the refractive index of the core be slightly higher than that of the clad glass. One thus needs to combine two glasses having similar properties, except for the refractive index. With the rod-in-tube method (Figure 5), the core glass is used for the rod and the clad glass for the tube: after strict adjustment of the rod into the tube, the preform obtained is drawn with a drawing tower and the fiber collected on a drum.

Figure 4 Comparison between the infrared transparencies of silica and fluoride fibers. Minima of the V-shaped curves of 1 dB/km for silica near the 1.55 μm telecom wavelength and of only 0.02 dB/km for fluoride at 2.9 μm .

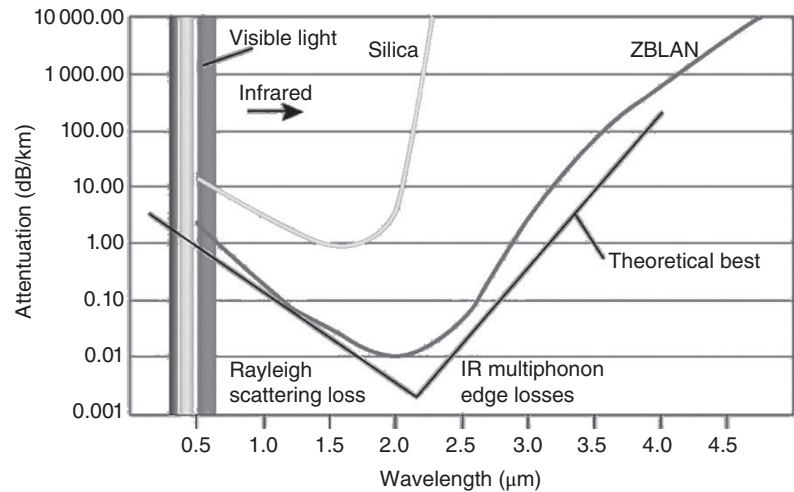
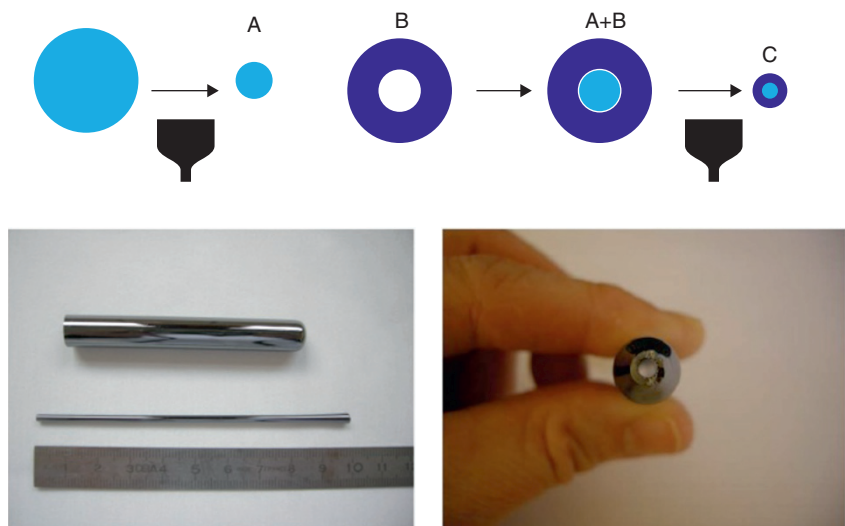


Figure 5 Production of a single-mode preform (C) from two Se–Te vitreous alloys: one for the core rod (A) and the other for the cladding tube (B). A as a first step, the rod has to be drawn into a stick to get the requested final diameter ratio.



4.3 Passive Properties

In passive functions the fiber transmits the light from a source toward a target [9]. Critical parameters are the spectral transmission window, the optical loss, and the resistance of the fiber to high densities of light especially when the source is a laser. Since silica fibers are both reliable and inexpensive, the only market left is the region where they are no longer transparent. The lowest optical losses are found around 3 μm before transparency begins to decrease strongly in the 4–5 μm region.

Single-mode fibers are used in very special sectors such as spatial interferometry in the spectral region beyond 2 μm where silica fibers become opaque. Although the intense research made on ultralow-loss fibers for telecommunications has declined, the potential for ultratransparency is still a reality. The lowest loss obtained

in the 1990s was about 1 dB/km around 2.9 μm , but higher transparency would be possible through reduction in the IR thanks to a cutoff that is slightly shifted toward longer wavelengths, at 5.5 instead of 4.6 μm for optical fibers. In practice, the composition of these glasses is also complex with molar concentration of InF_3 close to 50% and various heavy metal fluorides (BaF_2 , PbF_2 , ZnF_2 , GaF_3 , or CdF_2) to keep the phonon energy as low as possible and to prevent crystallization from happening. Besides, small amounts of alkali chlorides can be also added to adjust the refractive index.

4.4 Active Properties

When the core of a fluoride fiber is doped with luminescent rare earth elements, the device can be considered as a

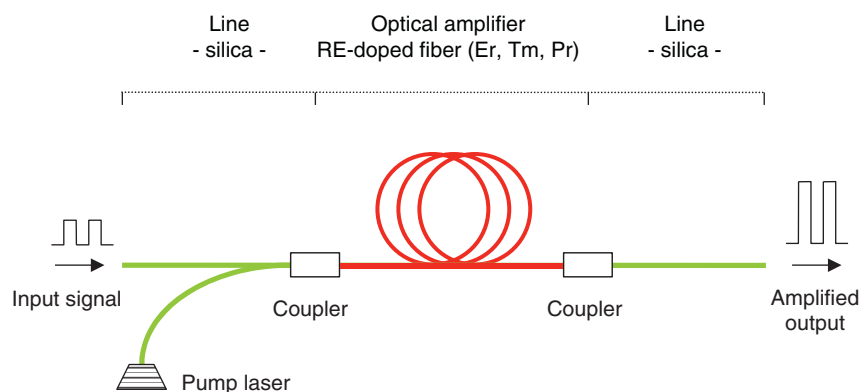


Figure 6 Optical configuration of a single-mode fluoride fiber used for laser action or optical amplification. Core glass doped with the appropriate rare earth ion.

new light source [4]. The optical configuration needs to be single mode to ensure the quality of the output light, whereas the specifications in terms of optical loss are as high as possible. The field was very active in the 1990s with the aim of developing two kinds of products, namely, optical amplifiers and fiber lasers. When a lanthanide is pumped with the appropriate source (a laser diode, for instance), the light emitted by the fiber is guided in its fiber, collected at the output (Figure 6), and serves to regenerate the telecom signal. For use as a laser, two mirrors are necessary to obtain the required oscillations.

The market of optical amplifiers is entirely driven by telecommunication constraints. Since the relevant wavelength is in the low-loss region of silica at $1.55\ \mu\text{m}$, the only rare earth operating in this region is the erbium ion Er^{3+} . Although the so-called erbium-doped fiber amplifier (EDFA) based on silica satisfies market needs thanks to their high efficiency, a potential for fluoride amplifiers resides in the use of other wavelengths located on the borderline of the silica low-loss region typically from 1.3 to $1.65\ \mu\text{m}$. Rare earth ions such as Pr^{3+} and Dy^{3+} are suitable for this region because the amplification ability is very poor in silica but very efficient in fluoride glasses. Compared with silica, however, a limitation of fluoride fibers is the impossibility of welding them with silica glass resulting from their chemical incompatibility.

Fiber lasers represent an expanding market because of their intrinsic advantages. Heat dissipation is, for instance, more efficient, whereas flexibility is fundamental to guide the light toward its target. The field is also dominated by silica fibers, which are strong and easy to prepare, but rare earths may have a weak luminescence in this matrix that suffers from poor transparency beyond $2\ \mu\text{m}$. Consequently there is some room for fluoride fiber lasers (Figure 7) as their emission range covers a broad spectral domain from UV to the mid-IR. The emission in the visible is due to *upconversion* or photon addition mechanisms, which are very efficient in this matrix.

Upconversion means that the ground-state electrons of the rare earth are first excited by photons pumped to an

upper long-life level. The same source can then promote these electrons to a higher level, from which light is emitted at wavelengths shorter than that of the pumping light. Pumping with an invisible IR source, for instance, results in the emission of a visible green light. Considering the power and the wavelength available from fluoride fibers (Figure 7), one sees that all these wavelengths are available for specific applications such as marking, cutting, or welding materials. Medical applications such as special surgery as well as analytical purposes are opening with this new kind of light sources

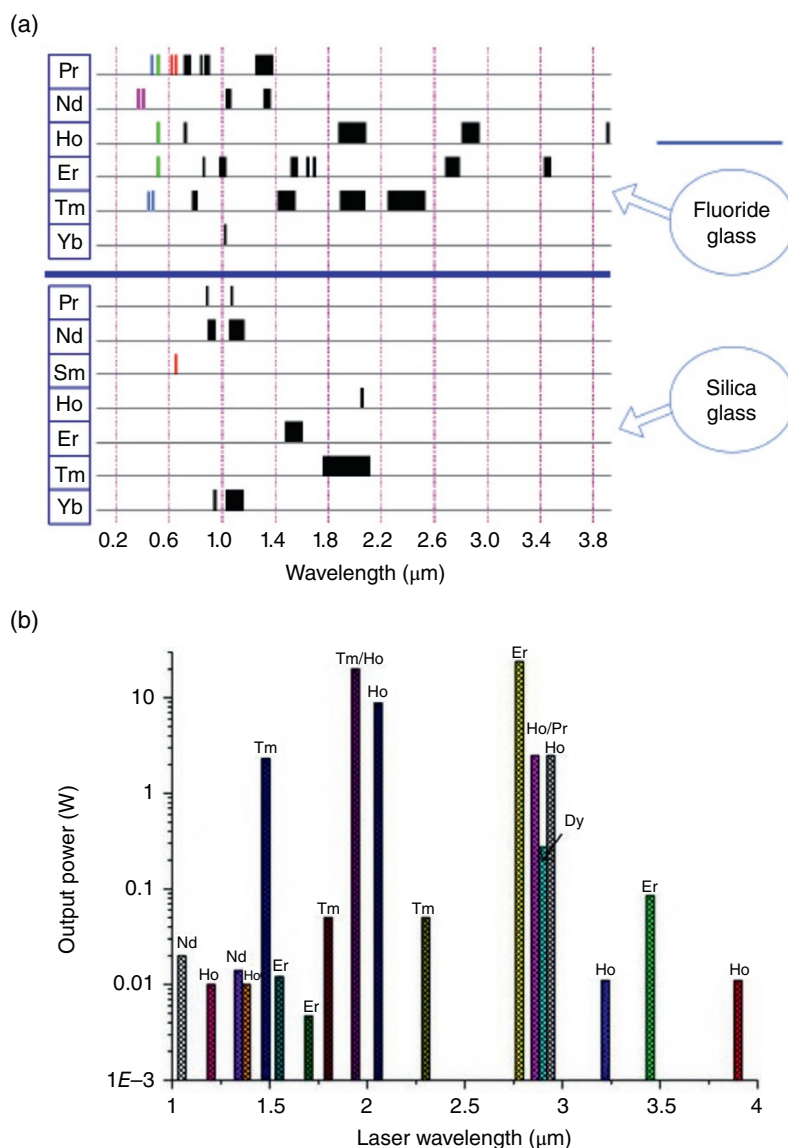
5 Chalcogenide Glasses

5.1 Formation with Chalcogens

Chalcogen glasses are built from S, Se, and Te, which lie below oxygen in the periodic table [6, 7]. Like oxygen, these elements are characterized by an outer electronic shell of six electrons, $s^2 p_x^2 p_y^1 p_z^1$, of which only the two odd electrons are involved in covalent bonding. Thus, these elements are generally twofold coordinated, generating crystal networks constituted of chains (Se and Te) or rings (S) in which the elements are strongly covalent bonded. The overall cohesion of these units is achieved through much weaker dipole–dipole van der Waals inter-chain bonds. Although the three chalcogens belong to the same family and share similar one-dimensional (1-D) crystal structures, they may be chemically “false friends” because sulfur and selenium are good glass formers whereas tellurium is not.

Although sulfur- and selenium-based glasses have similar chemistries, the former have a moderate interest because of their limited transparency in the mid-IR. Selenium thus is clearly the key element to form bulk glasses displaying the desired transparency in the mid-IR up to $16\ \mu\text{m}$. The strategies for glass formation are then the same as for fluoride in that they rely on empirical rules. The key ingredient is to form a polymeric melt with

Figure 7 Laser emission of rare earth-doped fibers. (a) Comparison between the emissions of fluoride and silica fibers. (b) Influence of the doping rare earth on the output power of fluoride fibers (from [6]).



highly flexible bond angles, thus yielding a floppy network keeping chemical bonds strong without periodicity.

In this respect, the structure of crystalline selenium is really unique as it is similar to that of an inorganic polymer. Its weak interchain bonds are easily broken by thermal agitation, hence a low melting point of 216 °C and the formation of a viscous liquid in which chain fragments persist. If Se is for this reason the only good glass-forming element, its glass transition temperature of 40 °C is much too low for any practical application. To increase it to ensure acceptable mechanical and thermal properties, a network dimensionality higher than 2 is required through chain cross-linking by elements close to selenium in the periodic table. In this way the covalent character of bonding is kept, and the strength of the structural network is improved. In practice, selenium chains are cross-linked

by trivalent elements such as As or Sb or tetravalent elements such as Ge, all of them having similar electronegativities. Two basic systems are then dominating the chalcogen-based glass scenery.

In the first (Se–Ge), the network is built with GeSe_4 tetrahedra connected to one another by Se chain fragments. The GeSe_2 composition yields a fully reticulated 3-D network where the tetrahedral units are directly corner shared. Because this stoichiometry is equivalent to that of SiO_2 in silicate glasses, one would expect GeSe_2 to be optimal in terms of viscosity and thermomechanical properties. On the contrary, its network is overconstrained because a lack of degree of freedom makes this glass difficult to form and unstable upon shaping. As for the GeSe_4 composition, its tetrahedral units are expected to be linked by Se–Se dimers providing the

needed flexibility to the network. As discussed in the Section 3.2, however, the structure of this glass is more complex, showing that chalcogenide chemistry may be complicated too.

In the second system (As–Se), the building blocks are AsSe_3 pyramids connected by bridging Se chain fragments. A fully reticulated network is obtained for As_2Se_3 , for which pyramids are expected to be directly linked by individual Se atoms. The resulting reticulated network has a 2-D planar shape and is floppy enough to provide a glass exhibiting good physical and rheological properties. This composition thus is one of the most widely used.

For technical and industrial uses, it is nonetheless advisable to oppose more strongly crystallization through more complex compositions bearing at least three elements. The so-called GASIR glasses belonging to the Ge–As–Se systems have, for instance, been developed by Umicore-IR glass company for molded IR optics. In these compositions the original 2-D planar network of the As–Se system extends into a third dimension through the GeSe_4 tetrahedral units incorporated, resulting in a T_g increase and in improved thermomechanical properties. The particular $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$ composition is the most stable selenide, which makes it matchless for molded IR lenses. Other interesting materials belong to the Te–As–Se system, where addition of tellurium aims at lowering the phonon energy to shift transparency slightly further in the mid-IR comparatively with a purely selenide glass. An example is the $\text{Te}_2\text{As}_3\text{Se}_5$ glass whose network is formed of mixed Te–Se chains reticulated by trivalent As. It is stable enough to be shaped by the DIAFIR company into optical fibers for mid-IR spectroscopy.

As for pure tellurium [1], its very poor vitrifiability originates in the marked metallic character of the bonds that ensure interchain cohesion, which is, for instance, indicated by an electrical conductivity several orders of magnitude higher for Te than that for Se. This metallic character also results in a delocalized π bonding cloud, shorter interchain distances, and stronger cohesion of the structure and, thus, in a melting point of 422 °C much higher than 216 °C of Se. As observed for alloys, Te liquid is constituted of isolated, unreticulated atoms, which is why a glass can be obtained only by splat quenching.

5.2 Network Reticulation from Selenium Chains

In technologically important selenide glasses, bonding is highly covalent with small coordination spheres: Se (two-fold coordinated), As (3), and Ge (4). Despite this apparent simplicity, the structure of a glass network was until recently understood more from the solid-state chemist's intuition than from hard experimental data. It was commonly described as a network of covalent bonds obeying the 8-N rule, but no consistent information had been

obtained on medium-range order, i.e. on the actual connection of the AsSe_3 and GeSe_4 polyhedral building blocks. The reason was that X-ray and neutron diffraction data are not easy to interpret in chalcogenide systems because the sizes of the electronic clouds and, unfortunately, also the neutron-absorption cross sections are very close to one another for Se, As, and Ge. And because these elements are neighbors in the periodic table, the Se–Se, Ge–Se, and As–Se bond lengths are too similar to allow structural organization to be determined from RDF. A decisive step was thus taken when the first ^{77}Se solid-state nuclear magnetic resonance (NMR) spectra were collected in the $\text{As}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{Se}_{1-x}$ systems [10].

For As–Se binary systems, NMR results have more or less confirmed the chemist's expectations (Figure 8). From pure Se to the famous As_2Se_3 , the network of Se-rich glasses evolves from a 1-D chain structure to a 2-D pyramidal network. For pure Se, it has in particular been confirmed that the structure is built from selenium chains, as found in crystalline phases, so melting does preserve the strong intrachain covalent bonds and only de-solder the chains in a disordered but still reticulated network. For As_2Se_3 , the glass structure as seen by ^{77}Se solid-state NMR is also very simple: each Se does directly bridge the AsSe_3 pyramids, whereas a transition to a structure with a lower dimensionality is observed at the As_2Se_3 stoichiometry, beyond which As-rich glasses are composed of a pyramidal backbone containing an increasing number of 0-D As_4Se_4 or As_4Se_3 units. This transition has a direct bearing on thermal and mechanical properties that, as exemplified by glass transition temperatures (Figure 8), exhibit a clear extremum at the As_2Se_3 composition, consistent with its technological interest.

For Ge–Se systems, selenium atoms embedded into chain or ring fragments can be clearly identified from the band assigned to Se– ^{77}Se –Se neighbors in the NMR spectra. The intensity of this line is expected to decrease from pure Se to GeSe_4 stoichiometry. At this point all GeSe_4 tetrahedra should be bridged by Se–Se dimers, so the NMR spectrum should exhibit a unique band assigned to Ge– ^{77}Se –Se neighbors. As collected by different authors, however, ^{77}Se NMR spectra completely disagree with such chemist's expectations. In particular, they reveal a large contribution of selenium-chain fragments that include at least 33% of the Se atoms. In other words, weak van der Waals bonds are abundant in the GeSe_4 network, which was expected instead to be fully 3-D. This feature is the reason why the thermal, mechanical, or optical properties of this material do not have any special interest with respect to other glasses of the $\text{Ge}_x\text{Se}_{1-x}$ system. In conclusion, no composition in the Ge–Se system plays a role similar to that of As_2Se_3 in the As–Se system. Because of the lack of sufficient

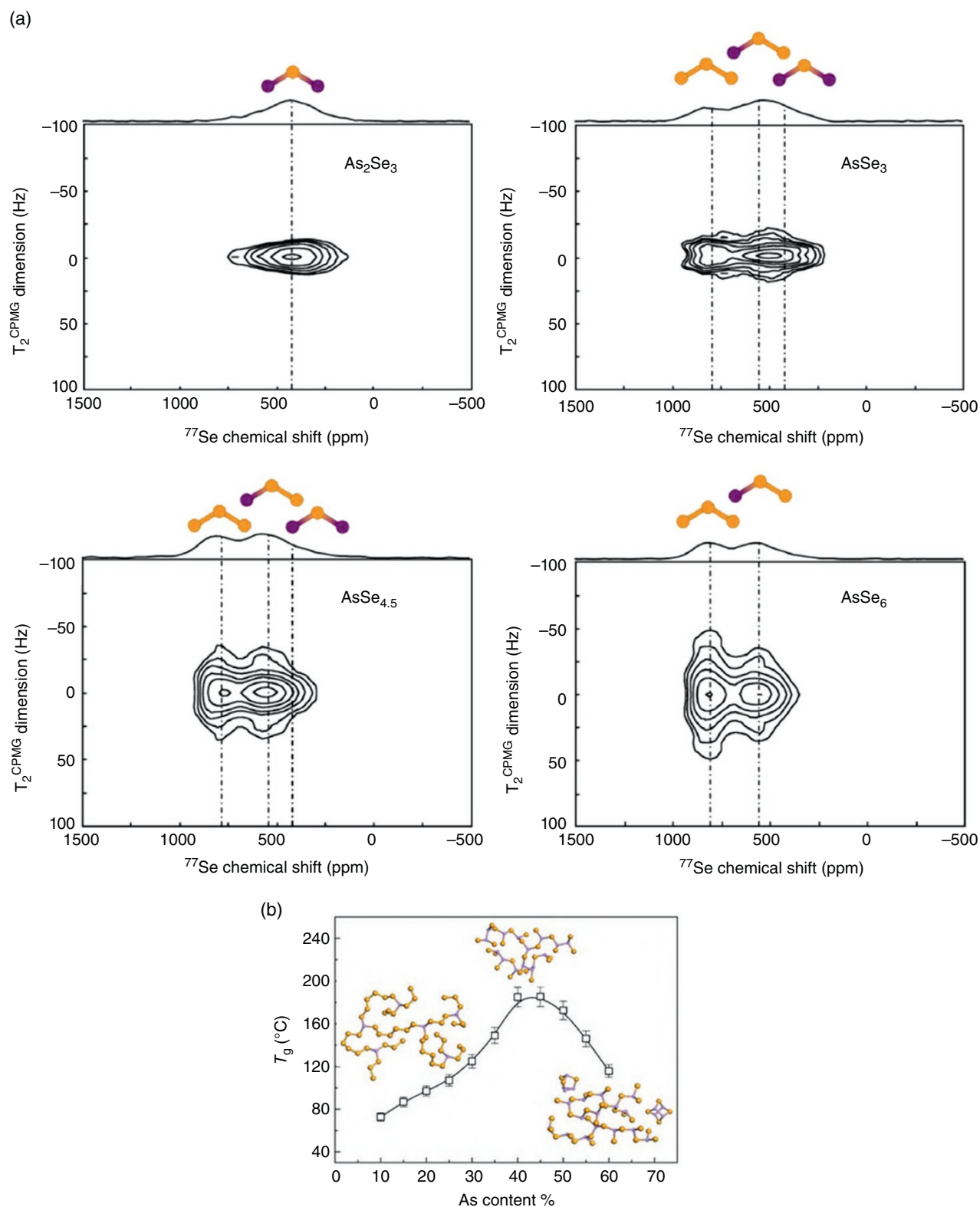


Figure 8 Structure of chalcogenide glasses as determined by solid-state NMR. (a) Bands assigned to Se– ^{77}Se –Se, As– ^{77}Se –Se and As– ^{77}Se –As neighbors, illustrating the monotonously increasing reticulation of the network with the As fraction x . (b) Variation of T_g with the dimensionality of the structural network: maximum value for the most reticulated network of As_2Se_3 , followed by a decrease at higher As contents where molecular units appear to destroy the covalent network.

chemical ordering, the physical and structural properties increase monotonously until the GeSe_2 composition is reached, which is not a good glass former.

6 Chalcogenide Glass Applications

6.1 General Considerations

Thanks to their more floppy network, chalcogenide glasses have in general an excellent resistance to devitrification as indicated by a lack of crystallization peak in their DSC thermograms. Their glass-forming region is wide enough that glasses having a suitable viscosity-temperature relationship can be selected for particular applications. A curve with a gentle slope is suitable for molding and fibering. Bonding is strong enough to ensure a good durability with respect to water corrosion. Nevertheless parasitic absorption bands are very common. They are due to contamination by oxygen atoms, which are detected in the multiphonon region. Also Se-H absorption bands in the 4–5 μm region are difficult to eliminate. Purification operations, which require special expertise, are thus of paramount importance during synthesis.

Finally, the glass transition of selenide glasses is directly connected to the dimensionality of the structural network. The richer the glass composition in reticulating elements (As or Ge), the higher the T_g . Whereas T_g is 40 °C for pure Se glass, it increases to 185 °C for the fully reticulated As_2Se_3 (Figure 8). For GASIR, which is enriched in Ge, it reaches 280 °C, making this glass composition suitable for application in hazardous condition as requested by the military. On the other hand, glasses with low T_g are easy to prepare but are not suitable for applications. They have in particular too high expansion coefficients, which translates into a real risk of network relaxation even at room temperature.

6.2 Infrared Glass Molding

One of the factors limiting mass production of thermal-imaging systems such as night-vision devices resides in the high cost of traditional IR optics. These are made from ZnS transparent ceramics or Ge single crystals

through expensive fabrication processes that include high-precision diamond turning to obtain the final product. In this respect glasses have the obvious advantage of being directly moldable to the desired shape. Chalcogenide glasses have indeed ideal rheological properties for molding operations at moderate temperature and pressure. With easily duplicated silica molds (Figure 9), complex aspheric and diffractive optical configurations can be produced with a quality that makes direct installation of the parts in an IR camera possible.

Generally speaking, the definite advantage of chalcogenide over fluoride glasses lies in their much wider transparency in the mid-IR. In fibers, this transparency extends to at least 11 μm for selenide glasses and even 16 μm for telluride glasses against only 5 μm for the best fluoride. Most applications are restricted to selenide glasses, however, because tellurides are prone to crystallize and difficult to shape [1–3].

Chalcogenide glasses belonging to the domain Ge-As/Sb-Se have best thermomechanical properties through addition of tetravalent germanium, which causes the glass transition to rise sharply to the 250–300 °C range. These glasses do not absorb light in the 3–5 and 8–12 μm optical windows where the atmosphere is transparent enough to transmit blackbody radiation. They are thus used to make lenses for IR cameras mainly designed for thermal imaging and night vision. Original developments were made for defense purposes, but the cost of these advanced optics is declining, making applications possible in many civilian areas such as assistance in night driving or fire-fighting, heat-loss detection for energy savings, or body thermal imaging in human and veterinary medicines. Compared with the previously used crystalline Ge lenses, optics molded from chalcogenide glasses are much cheaper thanks to the reduced cost of the starting material and the more simply implemented hot-pressing technology. Technologically optimized compositions include the GASIR 1 (standard) and GASIR 2 (including Sb instead of As) IR glass optics developed and commercialized by Umicore-IR glass (Table 1).

In photonic applications, partial crystallization in the form of nanocrystals and even microcrystals can be advantageous, particularly with regard to mechanical properties. But the nucleation and growth steps of the glass ceramization process must of course be strictly

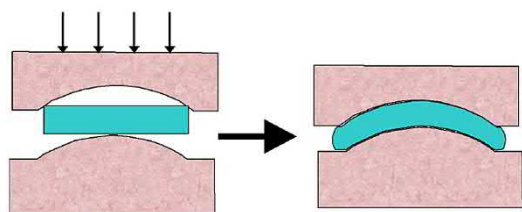


Figure 9 High-precision molding of chalcogenide glasses as lenses ready to be mounted in infrared optics.

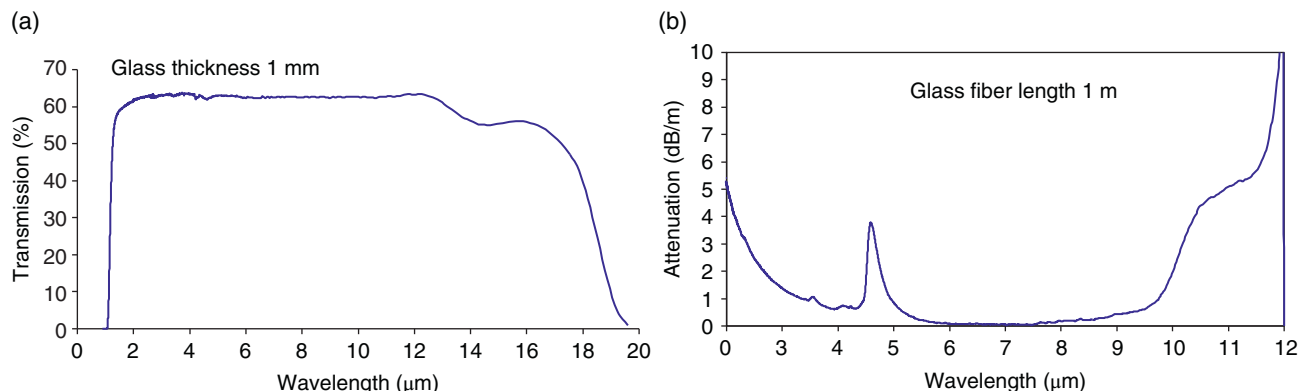


Figure 11 The outstanding optical properties a TAS (Te–As–Se) glass fiber in the entire mid-infrared range. (a) Transmission. (b) Attenuation. Main parasitic absorptions due to oxygen and hydrogen (see the Se–H residual band at 4.8 μm).

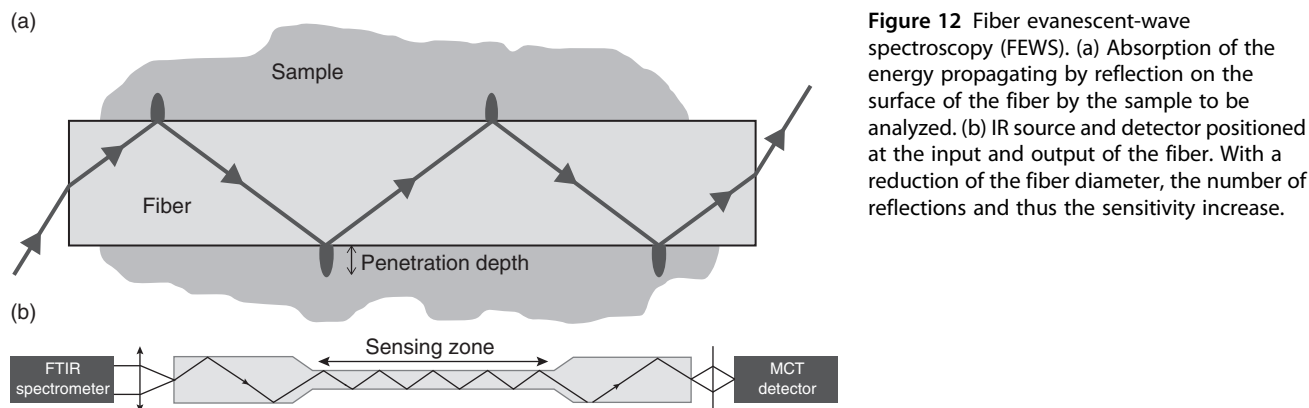


Figure 12 Fiber evanescent-wave spectroscopy (FEWS). (a) Absorption of the energy propagating by reflection on the surface of the fiber by the sample to be analyzed. (b) IR source and detector positioned at the input and output of the fiber. With a reduction of the fiber diameter, the number of reflections and thus the sensitivity increase.

States. Because the expected signs of life on exoplanets are the presence of water, ozone, and carbon dioxide in their atmosphere, the targeted signatures are the mid-IR absorption bands of these gases at 6, 9, and 15 μm for H₂O, O₃, and CO, respectively. For their detection by space telescopes, single-mode fibers transmitting light from 4 to 20 μm must be manufactured. Such TAS glass fibers, which are the first presenting a single propagation mode at 10 μm, have been successfully designed and fabricated by the rod-in-tube method (Figure 5). As they stand, they are suitable for detecting H₂O and O₃ but not CO₂, which absorbs at 15 μm [1, 2]. Such research programs thus are a unique and challenging incentive for the development of glasses transmitting as far as possible in the IR. This feature is exemplified by Te-based glasses, which are the only vitreous materials having so broad an optical window from 2 to 22 μm and, thus, collecting light so far into the IR. Independently of any market-driven motivation, these space programs do show that the search for new exotic materials should not

depend only on expected applications to remain a goal for researchers in materials science.

7 Perspectives

Chalcogenide glasses are a wonderful playground for exploring the optoelectronic properties of amorphous semiconductors. Although their applications are currently exploiting their transmission in the mid-IR, further effort in basic and technological research should lead to more sophisticated functionalities in photonics based on a coupling of their optical and electronic properties [11]. Chalcogenide glasses, for instance, have nonlinear properties about 100 times larger than silica because the electron cloud of heavy elements is much more polarizable than that of oxygen and also because of a large amount of lone pairs in the glassy network. These effects should allow for supercontinuum generation, i.e. for large

secondary sources emitting in the mid-IR induced by pumping of sharp laser source. This goal has already been achieved with fluoride glass, but the emission domain is then limited by the glass transparency to 4–5 μm . At this time, a strong research activity focuses on the realization of such sources from chalcogenide glass fibers or planar guides.

Chalcogenide glasses are characterized by many other fascinating light-induced phenomena such as photo-darkening, photo-fluidity, photo-expansion, and photo-crystallization [12, 13]. All of them are induced by photons and not by thermal agitation. In any case, the wavelength of the exciting source must be close to the band gap of the glass to create electron–hole pairs that change the nature of chemical bonds and coordination numbers, triggering local structural reorganization. These phenomena are observable in the bulk but are magnified for thin films.

Of interest is also the electrical switching effect, which was originally discovered in telluride glasses as a purely semiconducting phenomena. The very first application consisted in playing with the optoelectronic properties of selenium as amorphous thin film to develop electro-photographic devices. In these applications, however, devices based on crystalline silicon or amorphous silicon thin films have prevailed [7].

Especially within the ternary Ge–Sb–Te–Te system, Te alloys can vitrify as thin layers of nm thickness but only upon ultrafast quenching. Under laser-beam irradiation they undergo readily the glass to crystal phase transformation, so they are very good candidates for optical storage. Although the digital versatile disk (DVD) technology is based on the reflectivity contrast between the vitreous and crystalline phases, it might alternatively rely on electronic conductivity in view of the differences of several orders of magnitude between the properties of the two phases. In addition, a challenging research activity is underway to form stable glasses for optics based on tellurium, in particular for IR sensing. Finally, one may note that, thanks to their easy shaping, chalcogenide glasses and glass ceramics containing Li^+ as a mobile ion have also a high potential as solid-state electrolyte for the development of batteries (Chapter 9.5).

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6.6

Optoelectronics: Active Chalcogenide Glasses

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1 Introduction

From lenses and mirrors to optical fibers, glasses have traditionally been used as *passive* components in optics and photonics (Chapters 6.1, 6.4, and 6.5). But they can serve instead as spectral converters for *active* optoelectronic devices when they contain luminescent elements such as transition-metal and rare-earth ions. Among those active optoelectronic glasses, chalcogenides are unique because they are either used as matrices to host rare-earth ions or they constitute themselves luminescent sources in the form of the so-called quantum dots. Including from about 100 to 10 000 atoms in particles whose size ranges from several to tens of nanometers, these nanocrystals are incorporated in an amorphous matrix generally made up of silicate or phosphate glasses.

The first aim of this chapter thus is to present the most important features of rare-earth doped chalcogenide glasses for fiber-optic amplifiers and mid-infrared laser sources. As host materials, As–S, Ge–Ga–S, or Ge–Ga–Sb–Se chalcogenide glasses enhance the emission of light by rare-earth ions. The lifetimes of the excited electronic states of these ions depend much on whether or not their decays involve the simultaneous emission of multiple phonons. Because of their low-energy phonons, chalcogenide glass matrices thus ensure extended lifetimes for the excited electronic states of their host ions by making multiphonon relaxation difficult. Hence, they have potentials in fiber-optic amplifiers and mid-infrared lasers. The effect can be enhanced through addition of alkali halides such as KBr, KI, CsBr, and CsI to

chalcogenide glasses, in which cases a halide ion environment around a rare-earth ion further reduces electron–phonon coupling and, therefore, reinforce emission properties.

In the second part of the chapter, attention will be paid to quantum dots in transparent dielectric matrices. Because of quantum confinement effects, chalcogenide compounds such as CdS, CdSe, PbS, and PbSe present tunable optical properties when their size reduces to tens of nanometers. Glasses bearing quantum dots can thus cover a very wide range of wavelengths from the visible to the near-infrared, so they should give rise to universal fiber-optic amplifiers and color converters to be used in fields ranging from biomedicine (Chapter 8.4) to energy. Readers not familiar with these topics are referred to Chapter 6.5 for a detailed account on the structure and properties of chalcogenide glasses and to Chapter 6.3 for a review of spontaneous light emission in glasses.

2 Active Chalcogenide Glasses Doped with Rare-Earth Ions

Chalcogenide glasses doped with rare-earth ions have been considered as potential materials for mid-infrared lasers and fiber-optic amplifiers because of a low multiphonon relaxation compared with that of oxide glasses. This process competes against the desired emission, resulting in the reduction of the emission efficiency. It is more efficient in silica-based glasses whose intrinsic phonon absorption bands extend to the mid-infrared region. In contrast, chalcogenide glasses have relatively low phonon energies (Chapter 6.5, [1]) so that they can provide enhanced emission properties of certain fluorescence that are usually quenched in oxide hosts.

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In a pioneering work, As_2S_3 glasses were used as hosts of different ions such as Nd^{3+} , Ho^{3+} , Er^{3+} , and Tm^{3+} [2]. Successful incorporation of up to 2.0 wt % rare-earth ions was achieved. In addition, mid-infrared fluorescences were reported, for instance, at 2098 and 440 nm from the Dy^{3+} cascading transitions ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{13/2}$, respectively. Since then many other infrared emissions have been reported from Nd^{3+} and Ho^{3+} in sulfide glasses. Much effort has also been devoted to Ge–Ga (with As)–S and Ga–La–S glasses because of the high rare-earth solubility in these matrices, good glass-forming ability, and partial transparency in the visible spectrum. Indeed, infrared emissions have been observed upon doping of these glasses with Ho^{3+} , Tm^{3+} , or Dy^{3+} [3].

Recently, emissions in the telecommunication wavelengths have also been investigated for applications toward fiber-optic amplifiers. Chalcogenide glasses doped with Pr^{3+} and Dy^{3+} ions have proven interesting thanks to an original O-band centered near 1300 nm [4, 5]. Much effort is done to develop materials for amplifiers at short band (S-band) and wavelength regions outside of the conventional band (C-band).

3 Optical Fiber Amplifiers

3.1 O-Band (1260–1360 nm)

Telecommunication Window

The 1300 nm emission from Dy^{3+} or Pr^{3+} ions was first observed in 1994–1995 in doped $\text{Ge}_{25}\text{Ga}_{5}\text{S}_{70}$ (at. %) glasses that had been melt quenched [4, 5]. Although this transition of Dy^{3+} has a larger stimulated emission cross section than that of the ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$ transition in Pr^{3+} [5], it suffers from the short 38 μs lifetime of its upper emission level (${}^6\text{F}_{11/2}$, ${}^6\text{H}_{9/2}$) so that its quantum efficiency of 17% is low. This lifetime is in fact approximately one tenth of that measured from the ${}^1\text{G}_4$ level in Pr^{3+} because of the high multiphonon rate of 25 000 s^{-1} of its ${}^6\text{F}_{11/2}$, ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ transition in sulfide glasses.

These drawbacks have been remedied via the addition to the glass matrix of small amounts of alkali halides [6],

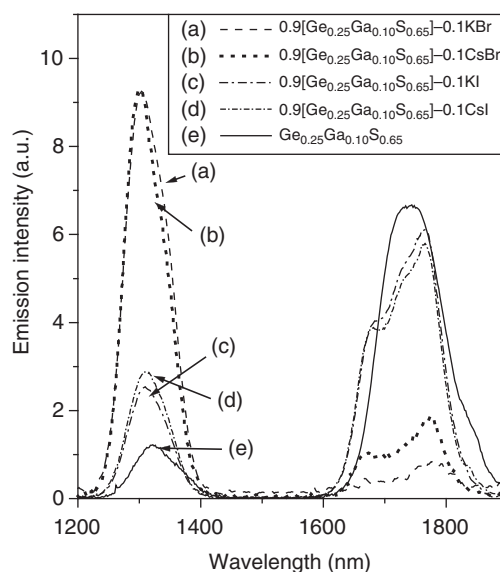


Figure 1 Effect of the nature of the alkali halide added on the emission spectra for the 1310 nm (${}^6\text{F}_{11/2}$, ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) and 1750 nm (${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{15/2}$) transitions in Dy^{3+} -doped chalcogenide and chalcohalide glasses [6].

which markedly enhance the intensity emitted by the transitions (${}^6\text{F}_{11/2}$, ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{15/2}$) at 1310 nm and (${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{15/2}$) at 1750 nm (Figure 1). As reported early [4], the intensity of the 1310 nm emission in Ge–Ga–S glasses is considerably smaller than that centered at 1750 nm. In alkali halide-bearing chalcohalide glasses, however, the 1310 nm emission intensity clearly increases at the expense of the 1750 nm fluorescence band. The lifetime of the ${}^6\text{F}_{11/2}$, ${}^6\text{H}_{9/2}$ level is 1320 μs , i.e. it is approximately 35 times longer than that measured from Ge–Ga–S glass with a quantum efficiency approaching 100% (Table 1).

3.2 S-Band (1460–1530 nm)

Telecommunication Window

Other interesting materials are thulium-doped glasses. These have been investigated for S-band (1460–1530 nm) amplifiers to make use of the 1480 nm

Table 1 Calculated (τ_R) and measured (τ_m) lifetimes and quantum efficiency ($\eta = \tau_m/\tau_R$) of the 1310 nm fluorescence band in 0.1 at % Dy^{3+} -doped chalcogenide and chalcohalide glasses [6].

	0.9[Ge _{0.25} Ga _{0.10} S _{0.65}] –0.1KBr	0.9[Ge _{0.25} Ga _{0.10} S _{0.65}] –0.1CsBr	0.9[Ge _{0.25} Ga _{0.10} S _{0.65}] –0.1KI	0.9[Ge _{0.25} Ga _{0.10} S _{0.65}] –0.1CsI	Ge _{0.25} Ga _{0.10} S _{0.65}
τ_R	840	964	326	317	205
τ_m	735	1320	220	193	36
η	0.88	>1	0.68	0.61	0.18

emission (Figure 2) from the $\text{Tm}^{3+}:^3\text{H}_4 \rightarrow ^3\text{H}_6$ transition [7]. Because the lifetime of the terminal emission level ($^3\text{F}_4$) is 8–10 times longer than that of the upper level, which hampers laser action, ways have been devised to achieve the required population inversion in Tm^{3+} ions, such as codoping with Ho^{3+} or Tb^{3+} ions [8]. As the energy gap between the $^3\text{H}_4$ level and the one located immediately below ($^3\text{H}_5$) is approximately 4300 cm^{-1} , the population of the $^3\text{H}_4$ level can alternatively be quenched through multiphonon relaxation. Glasses with low phonon energy must of course be used, namely, sulfides, fluorides [8], and tellurites [9]. But the amount of Tm^{3+} in glasses must be kept low, however, because the lifetime and population density of the $\text{Tm}^{3+}:^3\text{H}_4$ level is also quenched via cross relaxation ($^3\text{H}_4, ^3\text{H}_6 \rightarrow ^3\text{F}_4, ^3\text{F}_4$) when the Tm^{3+} concentration is high.

Chalcogenide and chalcogenide glasses containing CsBr provide viable solutions to these challenges. Three emission bands at 1220, 1480, and 1820 nm (Figure 2) are due to the $^3\text{H}_5 \rightarrow ^3\text{H}_6$, $^3\text{H}_4 \rightarrow ^3\text{F}_4$, and $^3\text{F}_4 \rightarrow ^3\text{H}_6$ transitions in Tm^{3+} , respectively. The 1480 nm emission intensity

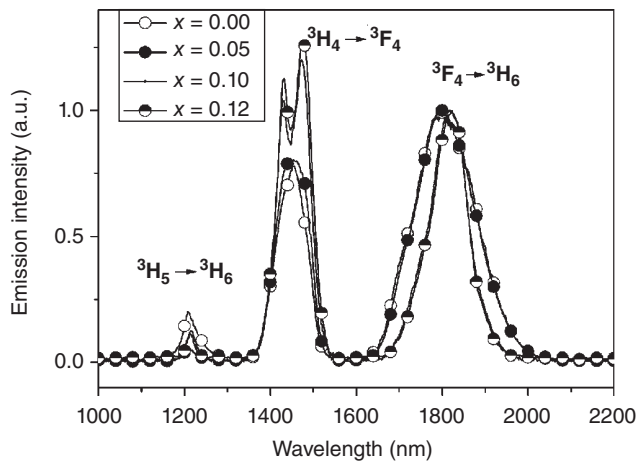


Figure 2 Effect of the CsBr fraction x on the emission spectra of Tm^{3+} in $(1-x)(\text{Ge}_{0.25}\text{Ga}_{0.10}\text{S}_{0.65}) \cdot x\text{CsBr}$ glasses. Tm^{3+} concentration of 0.05 mol % in all glasses [7].

increases sharply and the lifetimes of the $^3\text{H}_4$ level also increase rapidly from 0.23 to 1.23 ms upon CsBr addition (Table 2), whereas the measured lifetimes of the $^3\text{H}_4$ level decrease with increasing Tm^{3+} concentration in all glasses. In $\text{Ge}_{0.25}\text{Ga}_{0.10}\text{S}_{0.65}$ glasses, the $^3\text{H}_4$ level lifetimes, for example, decrease from 233 to 93 μs as the amount of Tm^{3+} increases from 0.05 to 0.50 mol %. These changes are due to the increased rate of cross relaxation ($\text{Tm}^{3+}:^3\text{H}_4, ^3\text{H}_6 \rightarrow \text{Tm}^{3+}:^3\text{F}_4, ^3\text{F}_4$) as the average distance between Tm^{3+} ions decreases. Therefore, the concentration of Tm^{3+} should be carefully optimized to prevent such large lifetime decreases.

3.3 U-Band (1625–1675 nm) Telecommunication Window

Another important ion is Ho^{3+} , which has several mid-infrared and visible emissions whose intensities markedly vary with the nature of the host material [3]. The 1660 nm emission from the $^5\text{I}_5 \rightarrow ^5\text{I}_7$ transition is usually quenched in oxide matrices as a result of strong multiphonon interaction because the energy gap between the $^5\text{I}_5$ and $^5\text{I}_6$ levels is only 2600 cm^{-1} . An intense 1660 nm band has nonetheless been achieved in several chalcogenide glasses [10]. A large gain is realized within the U-band window (1625–1675 nm) in sulfide glasses doped with Ho^{3+} and Tb^{3+} ions. Since gain coefficients are directly proportional to the quantum efficiency of the specific transition, selenide and chalcogenide glasses are attractive host materials thanks to their phonon vibration energies that are as low as 250 cm^{-1} .

Excitation to the $^5\text{I}_5$ level of Ho^{3+} with a 910 nm laser beam results in a dominant near-infrared fluorescence at 2000 nm ($^5\text{I}_7 \rightarrow ^5\text{I}_8$) and in two additional bands centered at 1660 and 1180 nm (Figure 3). With an increasing Ho^{3+} concentration, the intensity ratios between the latter two emissions ($I_{1.66\mu\text{m}}/I_{2.00\mu\text{m}}$) considerably decrease probably because of the cross relaxation ($^5\text{I}_5, ^5\text{I}_8 \rightarrow ^5\text{I}_7, ^5\text{I}_7$). The measured lifetime of the $^5\text{I}_5$ level is 9.38 ms (Table 3) for a high quantum efficiency of ~99%,

Table 2 Spectroscopic properties of Tm^{3+} in various glasses [6].

Host glass	$\text{Ge}_{0.25}\text{Ga}_{0.10}\text{S}_{0.65}$	$0.90(\text{Ge}_{0.25}\text{Ga}_{0.10}\text{S}_{0.65}) - 0.10\text{CsBr}$	Fluoride	Tellurite
Peak emission wavelength (nm)	1460	1480	1460	1450
FWHM (nm)	87	90	76	114
Measured lifetime (ms)	0.23	1.20	0.74–1.40	0.31
Quantum efficiency ($\tau_{\text{meas}}/\tau_{\text{rad}}$)	0.83	0.95	0.6–1.0	0.90
Emission cross section (10^{-20} cm^2)	0.54	0.14	0.18	0.36
$\sigma_e \times \tau_{\text{meas}}$ ($10^{-23}\text{ cm}^2 \cdot \text{s}$)	0.12	0.17	0.13–0.25	0.11

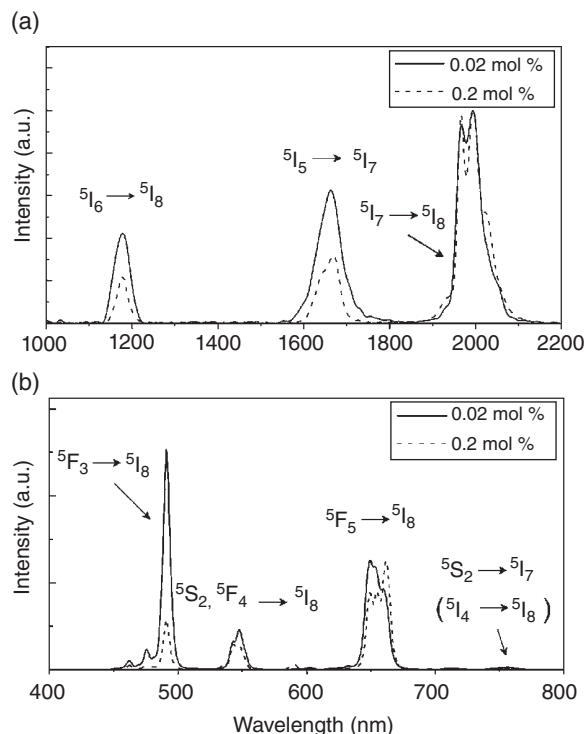


Figure 3 Effect of the Ho^{3+} concentration on the emission spectrum of doped 0.95GG51–0.05CsBr glasses. (a) Near-infrared region. (b) Visible region. Excitation wavelength: 910 nm. Emission intensities normalized to the intensities of the 2000 and 660 nm bands, respectively [10].

Table 3 Measured lifetimes (τ_m) of the Ho^{3+} : $^5\text{I}_5$ level at 293 K for chalcogenide glasses doped with different concentrations of Ho^{3+} . Radiative lifetime (τ_r) of the $^5\text{I}_5$ level of 9.44 ms as calculated from Judd–Ofelt analysis. Overall energy transfer rates (W_{ET}) obtained from $W_{\text{ET}} = 1/\tau_m - 1/\tau_r$.

Ho^{3+} concentration (mol %)	τ_m (ms)	W_{ET} (s^{-1})
0.02	9.38	1
0.05	8.41	13
0.1	6.18	56
0.2	4.16	134

which represents clear evidence for the aforementioned small phonon energy of chalcogenide glasses.

3.4 Rates of Multiphonon Relaxation

The degradation of the lifetime and quantum efficiency of excited electronic states is assigned to multiphonon relaxation. Its rate (W_{mp}) for energy gaps (ΔE) of 900–3500 cm^{-1} has been calculated from the ratios

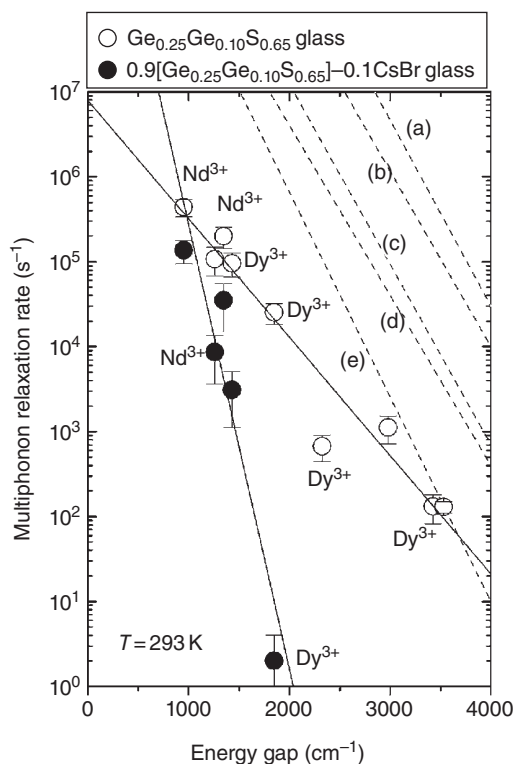


Figure 4 Dependence of multiphonon relaxation rates at room temperature on energy gap for phosphate: (a), silicate (b), germanate (c), tellurite (d), and fluoride (e) glasses. Solid lines: fits to the data calculated for Ge–Ga–S and Ge–Ga–S–CsBr glasses [7].

between the radiative and measured lifetimes. For sulfide and chalcogenide glasses (Figure 4), the ΔE and calculated W_{mp} data show the strongly beneficial effects of CsBr addition on both intensities and lifetimes. These data are described by the simple expression $W_{\text{mp}} = W_0 \exp(-\alpha \Delta E)$ where W_0 is the rate extrapolated to zero-energy gap and α a material-dependent constant. For both types of glasses, the rates for the excited levels are lower than found in oxide glasses by several orders of magnitude.

The temperature dependence of the multiphonon relaxation rates from the excited states of Dy^{3+} has been investigated to understand quantitatively changes in the local phonon mode. Up to approximately 150 K, the rates increase only slightly with temperature (Figure 5). At higher temperatures, they increase rapidly because of the stimulated emission of thermally activated phonons. Fits to the measured rates suggest that the five-phonon relaxation process of the 375 cm^{-1} vibration mode dominates in sulfide glass, whereas it is the six-phonon process of the 245 cm^{-1} vibration prevails in CsBr-bearing glasses (Figure 5a). Hence, these results strongly indicate that multiphonon relaxation originates in the stretching vibration of Ga–Br bonds in these glasses.

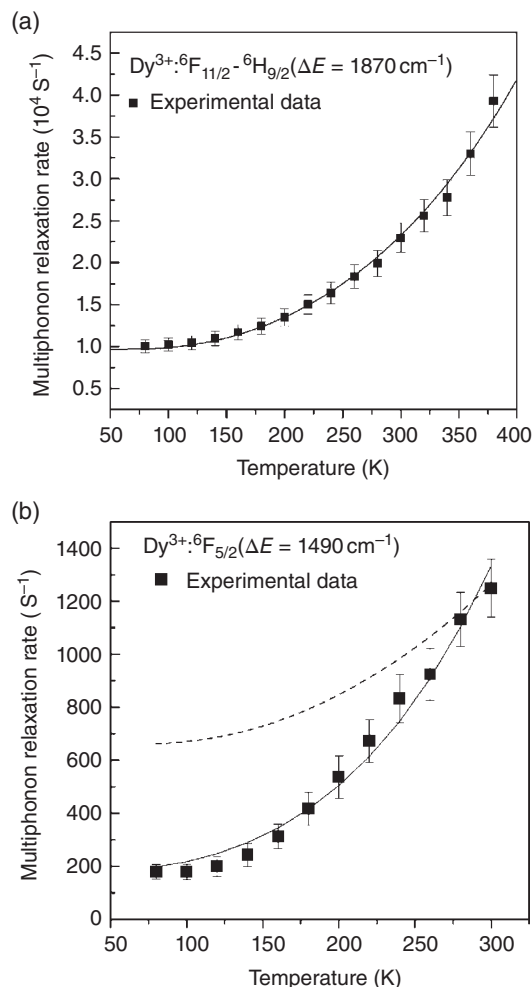


Figure 5 Temperature dependence of multiphonon relaxation rates in Dy³⁺ [6]. (a) From the ⁶F_{11/2}-⁶H_{9/2} level in Ge-Ga-S2 glasses. (b) From the ⁶F_{5/2} level in Ge-Ga-S2-CsBr glasses. Fits to the data made with five- or six-phonon relaxation processes.

3.5 The Influence of the Local Structure

Insights onto emission mechanisms can also be gained from studies of the local structure around the relevant ions, for instance, made with extended X-ray absorption fine structure (EXAFS) spectroscopy (Chapter 2.2). For Tm³⁺ ions, the L₃-edge EXAFS spectrum is similar in CsBr-bearing chalcogenide glasses and in crystalline TmBr₃. Representing the first neighbor shells around thulium in crystals, the main peak of the radial distribution function is observed at 2.74 (1) and 2.79 (1) Å (after phase correction) in TmBr₃ and Tm₂S₃, respectively (Figure 6). Because this peak becomes similar to that of TmBr₃ upon CsBr addition, one concludes that Tm³⁺ ions are mainly surrounded by Br⁻ ions in these chalcogenide glasses. From fits made to the EXAFS data, the sulfur coordination number of Tm³⁺ ions is in fact 6.77 (85) in Ge_{0.25}Ga_{0.10}S_{0.65} glass (Table 4). Upon addition of

CsBr, the first coordination shell around Tm³⁺ ions in contrast consists of ~5.86 (1.58) Br⁻ ions. This result again supports that the idea Tm³⁺ is predominantly surrounded by Br⁻ ions in CsBr-bearing chalcogenide glasses.

Large changes in emission properties upon CsBr addition suggest considerable modification of the local environment around rare-earth ions. The backbone of Ge-Ga-S glass is composed of edge- or corner-sharing GeS_{4/2} and GaS_{4/2} tetrahedra (Chapter 6.5, [11]). In CsBr-bearing glasses, Br⁻ ions seem to bond with Ga only. The bond energy is higher for Ga-Br than for Ge-Br whereas the bonding difference with S and Br is also larger for Ga than for Ge. Hence, Ga-Br bonds are energetically more favorable than Ge-Br so that the preferred coordination of Tm³⁺ ions with Br instead of S is likely related to the formation of [GaS_{3/2}Br]⁻ structural units in the glass matrix. In this case, [GaS_{3/2}Br]⁻ tetrahedral units need charge compensators, which are the rare-earth ions dissolved. These ions, therefore, ensure a reduced multiphonon relaxation and local refractive index compared with CsBr-free glasses, which significantly enhance emission properties [6].

4 Mid-Infrared Lasers

4.1 General Remarks

The mid-infrared range mostly refers to 3 000–25 000 nm wavelengths. It encompasses the atmospheric windows at 3 000–5 000 nm and 8 000–12 000 nm as well as the characteristic vibrational energy bands of most of gases, liquids and solids, including intermediate-reaction species and biological tissues (Chapter 6.5). Especially in the 3000–5000 nm interval, numerous mid-infrared laser sources have thus been studied for various applications including gas sensing, spectroscopy, chemical process monitoring, and military uses [11, 12].

Realistic high-power fiber lasers (>1 W) have been designed with Ho³⁺- or Er³⁺-doped ZBLAN optical fibers (Chapter 6.5), but they are operated at wavelengths shorter than 3000 nm where few applications are found. Although lasing above this wavelength is possible with ZBLAN glasses doped with Ho³⁺, Er³⁺, and Dy³⁺ ions, the high-power sources needed ensure only low outputs. Construction of a compact, high-powered, and economic all-fiber mid-infrared laser system is thus difficult with conventional fluoride glass fibers.

In this respect, chalcogenides are more advantageous than fluoride glasses. Not only are phonon energies lower than 350 cm⁻¹ for the former and higher than 500 cm⁻¹ for the latter, but chalcogenides show a wide transmission window extending to above ~10 000 μm. On the other hand, rare-earth ions such as Pr³⁺, Tb³⁺, Dy³⁺, Ho³⁺,

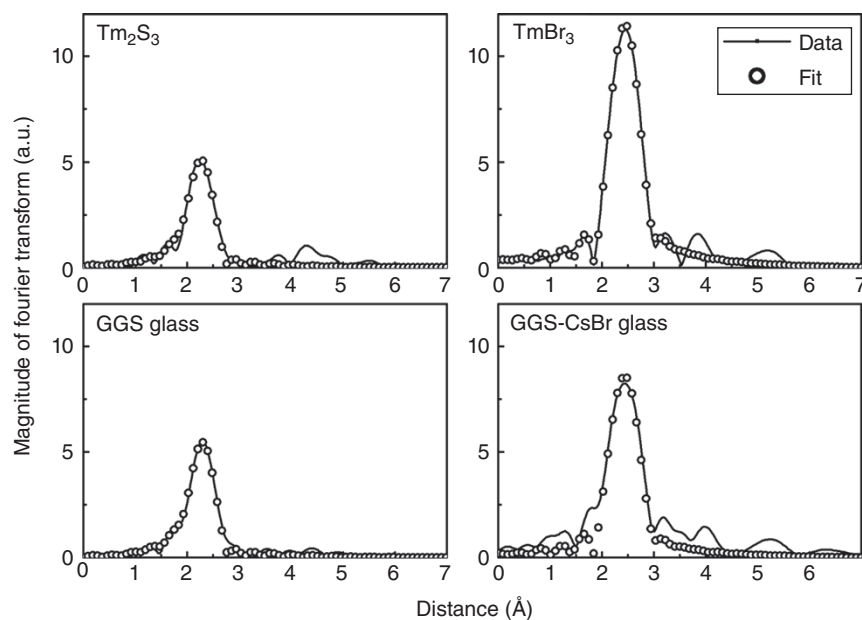


Figure 6 Radial distribution functions of Tm^{3+} ions determined from EXAFS results for the thulium sulfide and bromide crystals and the glasses indicated. Uncorrected phase shifts.

Table 4 Coordination numbers (N), bond distances (R), and Debye–Waller factors (σ^2) of Tm–S and Tm–Br bonds in crystals and glasses, along with the R -factors of the fits.

Bond	Composition	R (Å)	N	σ^2 (Å ²)	R -factor
Tm–S	Tm_2S_3 crystal	2.74 (1)	6.50 (fixed)	0.0115 (15)	0.013
	$\text{Ge}_{0.25}\text{Ga}_{0.10}\text{S}_{0.65}$ glass	2.77 (1)	6.77 (0.85)	0.0107 (14)	0.015
Tm–Br	TmBr_3 crystal	2.79 (1)	6.00 (fixed)	0.0066 (3)	0.001
	0.90 ($\text{Ge}_{0.25}\text{Ga}_{0.10}\text{S}_{0.65}$)–0.10CsBr glass	2.79 (1)	5.86 (1.58)	0.0083 (18)	0.020

Estimated uncertainties in parentheses.

Er^{3+} , and Tm^{3+} have $4f$ – $4f$ transitions whose wavelengths lie in the 3000–5000 nm range. When pumped to the $^6\text{H}_{11/2}$ state, dysprosium has in particular a strong emission near 3000 nm with a three-level lasing system. It has also an emission near 4300 nm, which suffers from a high multiphonon relaxation rate in other glass hosts. Praseodymium covers a wide 3500–5500 nm range but requires a suitable host matrix because of narrow energy gaps between its $|4f\rangle$ states ($<2500\text{ cm}^{-1}$). Practical mid-infrared emission from those ions has mostly been reported from selenide glasses [11, 13] whose phonon energies are even lower than 250 cm^{-1} .

4.2 Dy^{3+} -Doped Chalcogenide Glasses

The characteristic emissions of Dy^{3+} ion in $\text{Ge}_{30}\text{Ga}_2\text{Sb}_8\text{Se}_{60}$ selenide glass are observed upon excitation with a 1.8 nm pumping source (Figure 7). The broad and strong emission bands at 2900 and 4300 nm are attributed to the $^6\text{H}_{13/2} \rightarrow ^6\text{H}_{15/2}$ and $^6\text{H}_{11/2} \rightarrow ^6\text{H}_{13/2}$ transition of Dy^{3+} , respectively, thus proving their

potentials as mid-infrared activators. Absorption by atmospheric CO_2 during the measurement was also found at $\sim 4240\text{ nm}$ [11].

The emission is further improved via the introduction of sensitizers that can effectively transfer energy to the $\text{Dy}^{3+}:^6\text{H}_{13/2}$ state by absorbing the pumping radiation. Possible candidates are Pr^{3+} , Tb^{3+} , and Ho^{3+} . With a 2050 nm excitation source, the effect is by far the most important for the 2900 nm emission of Pr^{3+} (Figure 8), probably through energy transfer between the $\text{Pr}^{3+}: (^3\text{F}_2, ^3\text{H}_6)$ and $\text{Dy}^{3+}: ^6\text{H}_{13/2}$ states.

Such a potential is witnessed by emission spectra measured from selenide optical fibers either doped with Dy^{3+} (0.02 mol %) only or codoped with Dy^{3+} (0.02 mol %) and Pr^{3+} (0.05 mol %) ions (Figure 9). These core-only fibers 25 cm in length were prepared by a modified double-crucible method and mechanically spliced to silica fiber pigtailed pumping sources. Their mid-infrared emission was monitored by condensing the light to the monochromator with a band-pass filter and a mechanical chopper. The potential for fiber laser operating at the wavelength

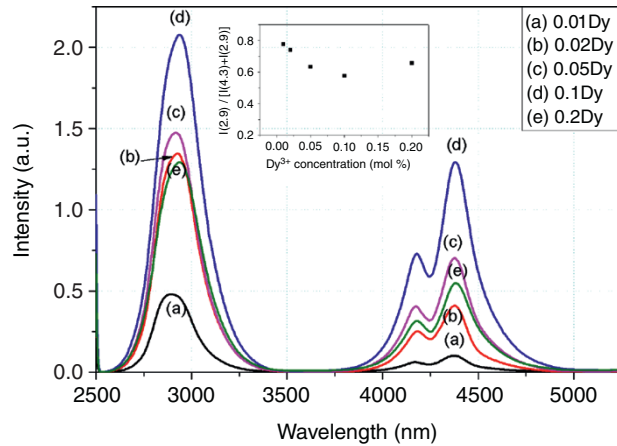


Figure 7 Emission spectra of Dy^{3+} in Ge-Ga-Sb-Se glasses for the concentrations indicated (mol %). Pumping wavelength of 1800 nm. Inset: ratio between the 2900 nm and total emission intensities against Dy^{3+} concentration.

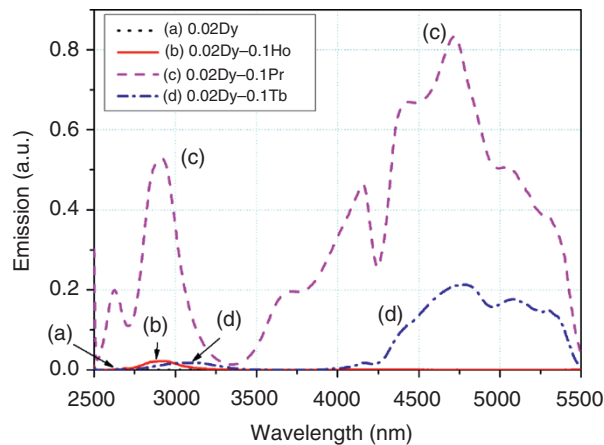


Figure 8 Effect of 0.1 mol % codoping on the emission spectra of Dy^{3+} -bearing Ge-Ga-Sb-Se glasses. (a) Dy^{3+} doping only at 0.02 mol %. (b) Codoping with Ho^{3+} . (c) With Pr^{3+} . (d) With Tb^{3+} . All glasses pumped at 2050 nm.

of about 3000 nm is clearly shown by the strong Dy^{3+} emission centered at around 2950 nm out of Dy^{3+} ion observed upon excitation at 1800 nm. Unlike in bulk glasses, the band near 4300 nm decreases in intensity because of the combination of CO_2 absorption with a long interaction length (25 cm). The spectrum of the fiber codoped with Pr^{3+} also differs from that of bulk glasses when pumped at 2050 nm. The emission near 2900 nm is then suppressed because of the energy relaxation from the $\text{Dy}^{3+} : {}^6\text{H}_{13/2}$ level back to the $\text{Pr}^{3+} : {}^3\text{H}_5$ state that is taking place along the fiber.

4.3 Pr^{3+} -Doped Chalcogenide Glasses

Strong and broad emissions due to radiative transitions of (${}^3\text{F}_2, {}^3\text{H}_6$) $\rightarrow$ ${}^3\text{H}_5$ ($\sim 3.7 \mu\text{m}$) and ${}^3\text{H}_5 \rightarrow {}^3\text{H}_4$ ($\sim 4.7 \mu\text{m}$) are observed from Pr^{3+} -doped selenide glasses (Figure 10). Absorption by CO_2 near 4240 nm also takes place. Hence, it must be corrected to obtain real emission spectra [14] in the 3000 and 5500 nm range, which is highly useful for broadband sources and gain media in the mid-infrared. The broadness of the ${}^3\text{H}_5 \rightarrow {}^3\text{H}_4$ emission is mostly due to the many Stark split manifolds along with site inhomogeneity within the host matrix. In fact, the emission bandwidth increases with the Pr^{3+} concentration except for the one centered at around 3700 nm because of increased interaction among the excited states of Pr^{3+} ions. The measured fluorescence lifetime of the $\text{Pr}^{3+} : {}^3\text{H}_5$ state in selenide glasses is longer than 4 ms (Figure 10). Upon incorporation of Pr^{3+} ions, it displays a maximum at 0.02 mol % and then decreases. One has assigned this initial lifetime increase with Pr^{3+} concentration to increases of the population of the electronic ${}^3\text{H}_5$ states by cross-relaxation processes and the following decrease to energy transfer between Pr^{3+} ions made possible by reduced interionic distances. For practical use of Pr^{3+} ion as a mid-infrared activator, a compromise between lifetime

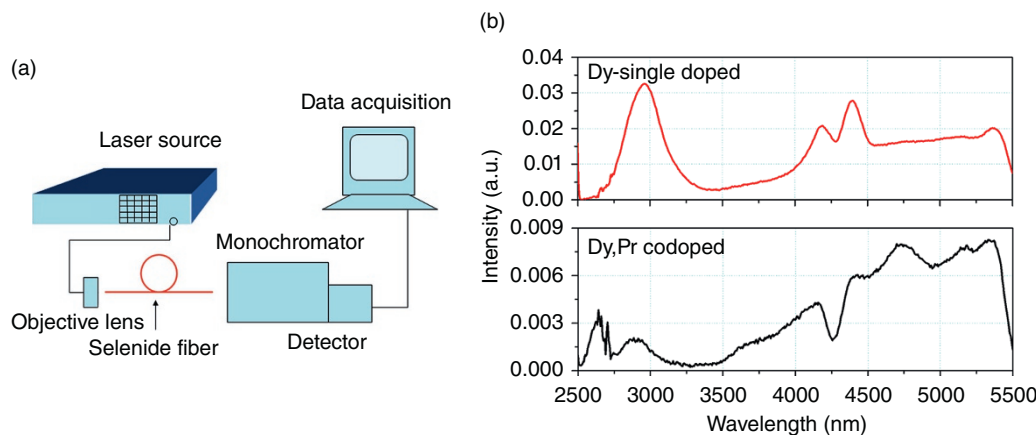


Figure 9 Emission measurements on a Ge-Ga-Sb-Se fiber doped with 0.02 mol % Dy^{3+} . (a) Experimental setup. (b) Effect of 0.05 mol % Pr^{3+} codoping on the emission spectrum (upper diagram: 25 cm fiber length and 1800 nm excitation; lower diagram: 15.5 cm and 2050 nm).

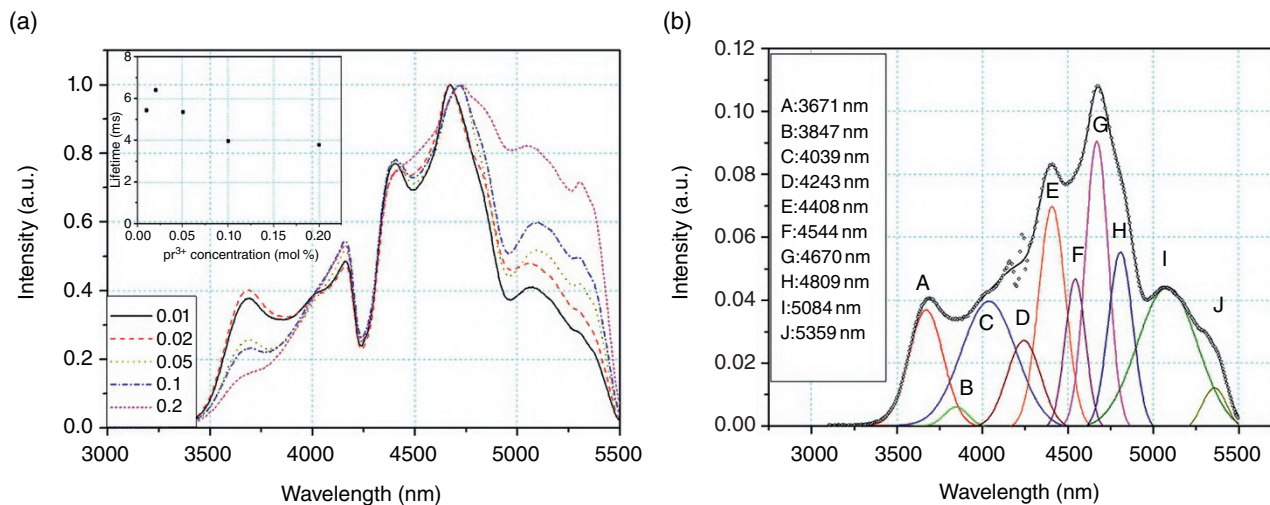


Figure 10 Emission spectra of Pr³⁺ singly doped Ge–Ga–Sb–Se glasses. (a) Effect of Pr³⁺ concentration (mol %) upon pumping at 2050 nm; intensities normalized to their maximum values. Inset: Pr³⁺ concentration on the lifetime of the Pr³⁺:³H₅ state. (b) Peak deconvolution of the mid-infrared radiative transition of Pr³⁺ after correction for CO₂ absorption [14].

and bandwidth must be reached. Suitable doping concentration of Pr³⁺ in Ge–Ga–Sb–Se glass could, for instance, be 0.02–0.05 mol % to avoid these interactions between Pr³⁺ ions (Figure 10).

As already noted for Dy³⁺, mid-infrared emission by Pr³⁺ may be further enhanced by sensitizers such as Tm³⁺ and Ho³⁺ ions, which have similar absorption bands around 2000 nm. These do not have any lying energy levels lower than that of the Pr³⁺:³H₅ state, which can eliminate possible back energy transfer from Pr³⁺ ions that would enhance the quantum efficiency of the Pr³⁺:(³F₂, ³H₆) and ³H₅ states. In the emission spectra recorded from codoped selenide glasses (Figure 11), noticeable improvement is achieved with Tm³⁺. The highly efficient energy transfer from the sensitizer ion is due to the strong thermal coupling between the Tm³⁺:³F₄ and Pr³⁺:(³F₂, ³H₆) states along with the high absorption cross section of the Tm³⁺:³F₄ state. Upon pumping at 2050 nm, Ho³⁺ on the contrary decreases the mid-infrared emission of the Pr³⁺:(³F₂, ³H₆) level in spite of its energetic closeness with the Ho³⁺:⁵I₇ state. The effect can be attributed to a back energy transfer from the Pr³⁺:(³F₂, ³H₆) to the Ho³⁺:⁵I₇ level suppressing the radiative emission intensity. The lifetime of the 4700 nm emission decreases in the presence of Ho³⁺, but, consistent with the sensitizer effect, no considerable change is observed with Tm³⁺-codoped samples. In summary, these results point to a high potential of Pr³⁺/Tm³⁺-codoped selenide glasses as a mid-infrared gain media in the 3500–5500 nm region.

The feasibility of a fiber-gain medium has been also examined with the aforementioned optical fibers doped with 0.02 mol % Pr³⁺ [15]. For this purpose, experiments

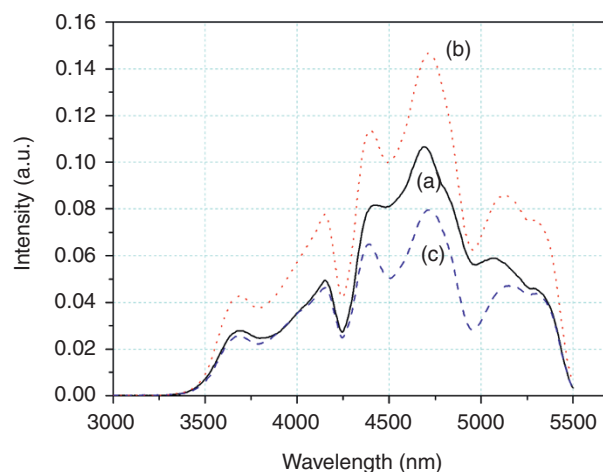


Figure 11 Effect of codoping on the emission spectra of selenide glasses doped with 0.05 mol % Pr³⁺. (a) Starting glass. (b) Codoping with 0.2 mol % Tm³⁺. (c) With 0.2 mol % Ho³⁺. All glasses pumped at 2050 nm [14].

have first been made with a 1480 nm laser diode and a 2050 nm fiber laser to design the proper pumping scheme. The emission spectra then obtained are similar to those of the bulk glass, indeed proving the potential of the fiber as a gain medium when pumped at these two wavelengths (Figure 12). Upon pumping at 1480 nm, the emission peaks at around 5250 nm as determined by the second-order emission of the (³F₃, ³F₄) → ³H₅ transition. Pumping at 2050 nm is more favorable for the fiber laser, however, because of the distinct emission near 4700 nm and the detrimental effects of the 1480 nm excitation. When the fiber is excited up to the (³F₃, ³F₄) manifold, an excited-state absorption to ¹G₄ and other

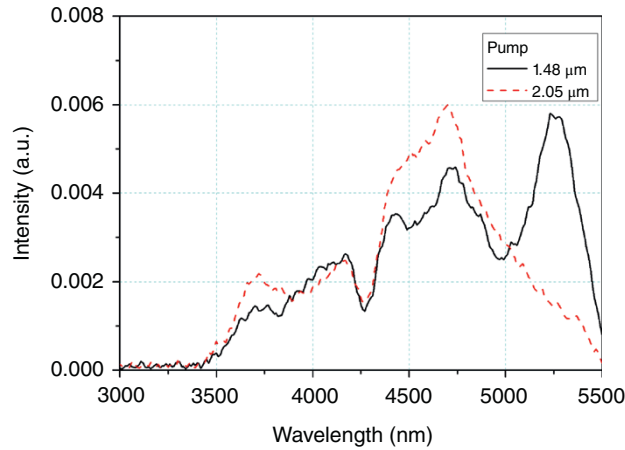


Figure 12 Influence of the pumping wavelength on the fluorescence emission spectrum of a selenide optical fiber doped with 0.02 mol % Pr^{3+} [14].

higher-lying energy levels is likely to happen and to cause a depopulation of the $^3\text{H}_6$ and $^3\text{H}_5$ levels and, thus, to hamper gain development in the mid-infrared range. In any case, absorption by defects such as Ge—H (~ 4950 nm) and Se—H (~ 4500 and ~ 4750 nm) [11] can seriously impair the lasing action when a longer interaction length is required to improve the accumulated stimulated emission. Such impurities should thus be removed during glass and fiber fabrication through controlled refinement processes. Atmospheric contamination of the selenide fiber must also be avoided via passivation of the fiber with proper jacket materials.

5 Chalcogenide Quantum Dots

5.1 Fundamentals

Semiconducting CuCl, CuBr, CdS, and CdSe nanocrystals were first grown in a glass matrix by A. Ekimov and coworkers [16]. Since then, original quantum properties have prompted the synthesis of these new materials in colloidal solutions and, especially, the exploitation of the fact that changes in the size of chalcogenide quantum dots allow their spectral region to be widely tuned from the visible to the mid-infrared region. For optoelectronic applications, chalcogenide (CdX, PbX, X = S, Se, and Te) quantum dots are best incorporated in glasses, which possess themselves unique optical properties, high durability, easy processability, and compatibility with existing optical products.

When the sizes of semiconductor nanocrystals are comparable or smaller than the radius of their electron–hole pairs (i.e. their Bohr exciton), electrons and holes confined in all three spatial dimensions experience discrete energy states caused by confinement effects

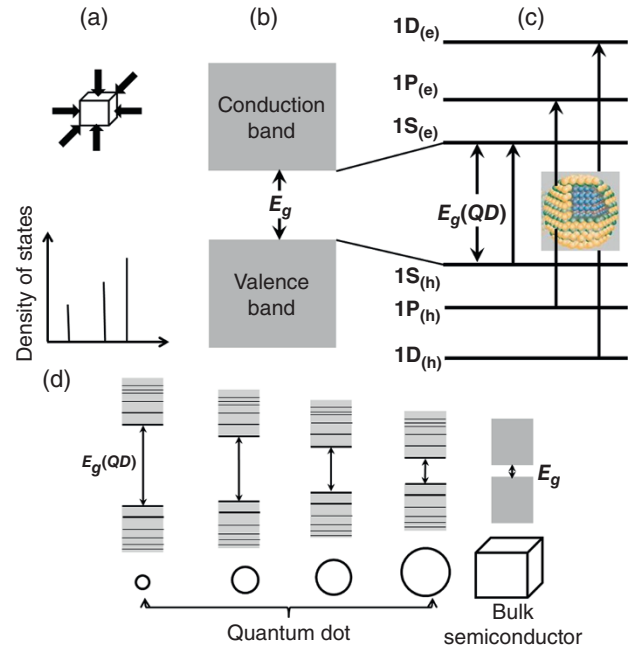


Figure 13 The physics of a semiconducting quantum dot. (a) Zero-dimensional structure and density of state. (b) Continuous conduction and valence energy bands of a bulk semiconductor separated by a fixed energy gap, E_g . (c) Discrete atomic-like states energy levels of the quantum dot. (d) Influence of particle size on the band-gap energy [$E_g(\text{QD})$].

(Figure 13a). In a quantum dot, this confinement leads to a collapse of the continuous energy bands of the bulk material (Figure 13b) into atomic-like discrete energy levels (Figure 13c) whose well-separated states can be labeled with an atomic-like nomenclature (1S, 1P, 1D, etc.). As the quantum dot size increases, the band-gap energy also decreases (Figure 13d), resulting in a shift of the absorption and emission wavelength. These nanometer-sized semiconductor crystals are thus kinds of artificial atoms, which bridge the gap between cluster molecules and bulk materials.

As defined by the gap energy of the lowest exciton transition, the effective band gap $E_g(\text{QDs})$ can be estimated from the parabolic effective mass approximation [17]:

$$E_g(\text{QDs}) = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R}. \quad (1)$$

In the first term, R is the radius of spherical quantum dots and E_g the band-gap energy of their bulk counterparts; in the second, the quantum confinement localization for electrons and holes is described in terms of m_e^* and m_h^* , the electron and hole effective masses, respectively; in the third, the Coulombic attraction, which is determined by the dielectric constant (ϵ), is negligible. Hence, the band-gap energy is simply proportional to $1/R^2$.

Table 5 Bohr exciton radii (a_B), band-gap energies (E_g), and wavelengths (λ) of the band-gap energies of CdX and PbX (X = S, Se, and Te) bulk semiconductors.

Semiconductor	a_B (nm)	E_g (eV) at 300 K	λ (nm)
CdS	3	2.53	490
CdSe	6	1.74	713
CdTe	7	1.50	827
PbS	18	0.41	3024
PbSe	47	0.28	4593
PbTe	50	0.31	4000

These data are summarized in Table 5 for bulk chalcogenide semiconductors. Because of small Bohr exciton radii and relative large band-gap energies, CdX quantum dots usually show a medium confinement and ensure tunable wavelengths in visible parts of the spectrum through a surface effect. In contrast, PbX semiconductors possess large Bohr exciton radii and narrow band-gap energies, resulting in a strong confinement and tunable wavelength in the near-infrared with a smaller surface effect.

5.2 Optical Properties of Quantum Dots in Glasses

As quantum dots get smaller, their effective band-gap energy increases. As a result, the exciton transition shifts to shorter wavelengths, which offers a convenient way to tune their absorption and photoluminescence wavelengths through size changes. In a silicate glass containing PbS quantum dots of different sizes (Figure 14), the onset of light absorption shifts from ~ 1000 to ~ 2000 nm when the radius increases from 1.9 to 4.6 nm. Relative to the lowest absorption peak (Figure 14b), the emission undergoes a Stokes shift to the red with the same tunability. Theoretical work has been done to account for the dependence of the band-gap energy on the particle size in terms of a parabolic effective mass mode, Eq. (1), a hyperbolic-band approximation, a tight-binding model, or an envelope wave-function calculation.

In addition to size, external fields such as temperature can also influence the band-gap energy. For virtually all semiconductors, the temperature dependence of the band-gap energy is well known experimentally. It includes contribution from the lattice thermal expansion and electron–phonon interactions in bulk semiconductors, but depends strongly on particle size. Both effects become insignificant when the energy levels are determined more by the structure than by the lattice constants and the spacing between the quantum-confined energy

levels increases. For the lowest exciton energies of PbS quantum dots of different sizes in glass and polymer matrices, the dE_g/dT measured from 12 to 300 K is actually almost zero for the smallest particles and approach the bulk value of $\sim 500 \mu\text{eV/K}$ only for largest [18]. The temperature independence of the energy gap for the smallest dots thus is a direct consequence of strong quantum confinement.

Owing to high surface to volume ratios, unsaturated or dangling bonds at the particle surface act as surface traps for charge carriers. As a consequence (Figure 15), electron and hole pairs recombine not only directly within quantum dots (Band I of the photoluminescence spectrum) but also on surface traps, resulting in nonradiative or deep trap emission on the low-energy side of the band edge (Band II). Because of the small Bohr radius of CdS, a two-band photoluminescence can be easily observed in the room-temperature spectrum of this quantum dots in a silicate glass. When the particle size increases, the intensity of trap emission decreases as surface atoms become relatively less numerous.

To reduce surface trap states, dangling bonds at the surface of quantum dots must thus be passivated. Trioctylphosphine oxide $[\text{OP}(\text{C}_8\text{H}_{17})_3]$, TOPO and trioctylphosphine $[\text{P}(\text{C}_8\text{H}_{17})_3]$, TOP are the most frequently used organic passivating groups for CdSe. Passivation of surface defects can also be achieved with the deposition of an inorganic shell semiconductor onto the core quantum dots in the so-called core/shell structures. The shell material then has a wider band gap than the core quantum dots, also enhancing carrier confinement. It is difficult to passivate the entire surface of quantum dots in a glass, however, so surface effects remain significant and result in a lower luminescence efficiency. A quantum yield as high as 50% has nonetheless been achieved recently for CdSe/ $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ core/graded shell quantum dots [19] and for CdS/ $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ sandwich-structured quantum dots [20] in glasses, whereas an efficient intrinsic emission from CdSe and CdS nanocrystals was observed.

5.3 Fabrication of Glasses Containing Quantum Dots

5.3.1 Methods and Matrices

Quantum dots mainly form in glasses through the decomposition of solid solutions that become oversaturated. In the most convenient and inexpensive method, the glass batch and semiconductor are mixed and melted at high temperatures to form a precursor glass, which is then annealed near or above the glass transition. These treatments promote the nucleation and diffusion-controlled growth of semiconducting nanocrystals (Chapter 5.4) and cause the absorption and

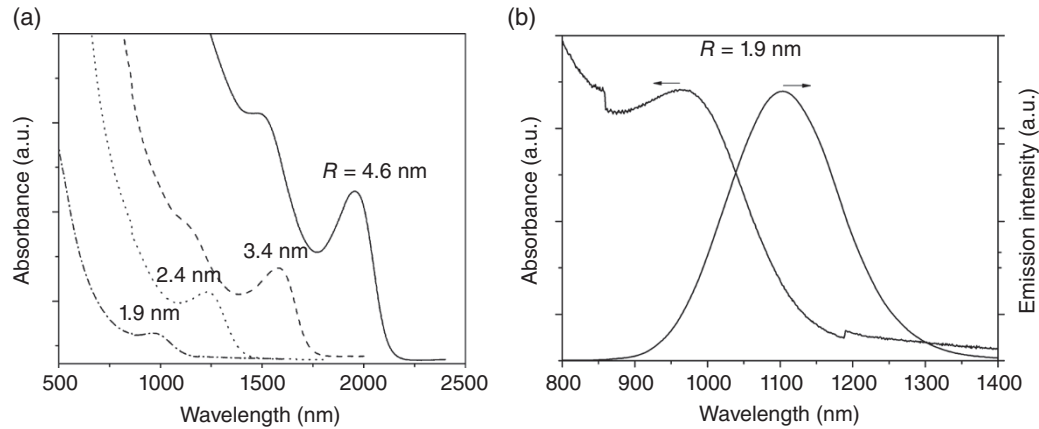


Figure 14 Absorption spectra of PbS quantum dots in a silicate glass. (a) Shift toward higher wavelengths with increasing particle size (1.9–4.6 nm). (b) Absorption and photoluminescence spectra for an average particle radius of 1.9 nm.

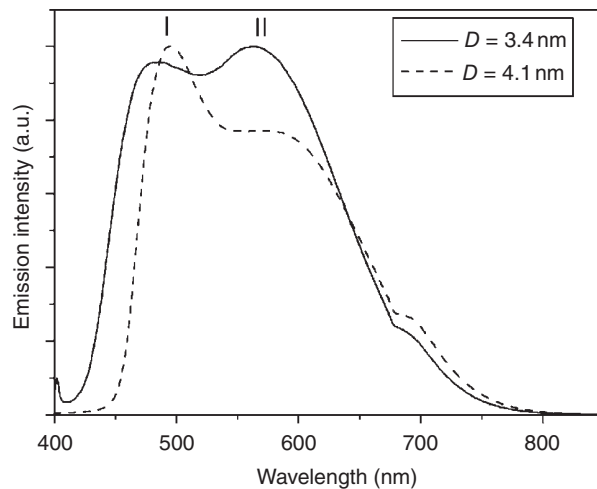


Figure 15 Two-band photoluminescence of CdS quantum dots in a silicate glass. Room-temperature spectra for 3.4 and 4.1 nm particles.

photoluminescence peaks to shift with higher temperatures or longer process durations (Figure 16) [21].

The solubility of chalcogenides is smaller than ~1 mol % and about 5 mol % in silicate and phosphate glasses, respectively (Table 6). The former matrices are most frequently used because of their high durability and easy processability. Because the glass batch is then typically melted above 1300 °C, some extra chalcogenide is added to compensate for partial volatilization. Alternatively, phosphate matrices are selected to increase the concentration of chalcogenides and reduce their volatilization at lower melting temperatures of about 1100 °C before annealing at around 400 °C. Owing to higher solubilities and ion mobilities, however, the growth of quantum dots is more difficult to control in phosphate than in silicate glasses.

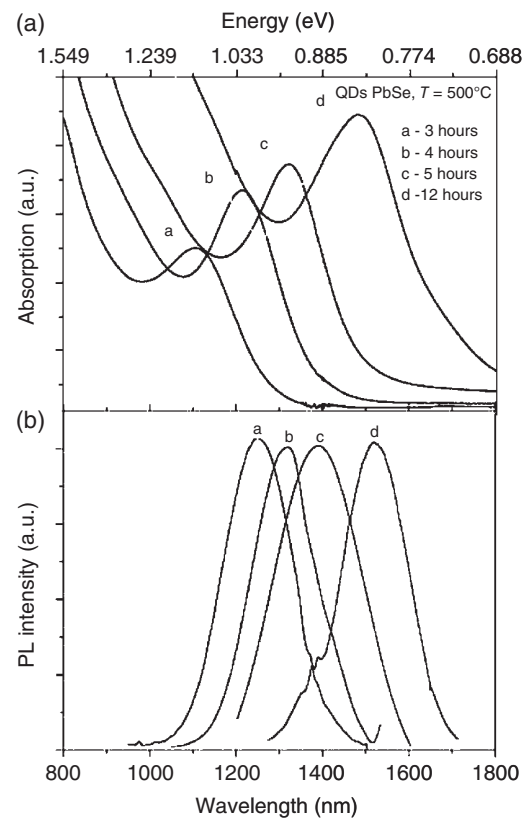


Figure 16 Room-temperature optical properties of PbSe quantum dots in a glass. (a) Absorption spectrum. (b) Photoluminescence spectrum. Average particle diameters of 4.9, 5.3, 5.8, and 6 nm for samples a, b, c, and d, respectively, all annealed at 500 °C [20].

Two other techniques have been developed for incorporating quantum dots in glasses. With sol–gel methods (Chapter 8.2), the most efficient manner is to prepare quantum dots by a colloidal technique and to introduce them in the sol before aging or deposition as a

Table 6 Compositions and preparation of PbS-, PbSe-, and PbTe-doped glasses.

Glass	QD	Batch (wt %)	Melting	Annealing
Silicate	PbS PbSe	SiO ₂ (59.1)	1350 °C	500–575 °C
		Na ₂ O (14.6)	3 h	0.5–16 h + 550–625 °C
		Al ₂ O ₃ (4.16)		0.5–1.5 h
		ZnO (14.8)		One- and two-step
		PbO (3.87)		
		F (1.93)		
		S/Se (1.45)		
	PbS	SiO ₂ (56)	1200 °C	550–625 °C
		B ₂ O ₃ (17.3)	2 h	30 min to several days + 625–700 °C
		Na ₂ O (9.63)		A few min to several h
		Al ₂ O ₃ (6.33)		Two-step
		CaO (8.71)		
	PbTe	PbS (2)		
		SiO ₂	1350 °C	525 °C
		Na ₂ O	50 min	20–90 min
		Al ₂ O ₃		One-step
		ZnO		
Phosphate	PbS PbSe	PbO (1.5)		
		Te (1.5)		
		P ₂ O ₅	1100–1150 °C	390–440 °C
		Na ₂ O	Closed crucible	Several min to 2 h
		ZnO		One-step
		AlF ₃		
		Ga ₂ O ₃		
		PbS/PbSe		

See [22] for cadmium chalcogenides.

silica-doped film. But bulk glasses cannot be obtained in this way. Ion implantation is another surface method. Quantum dots form upon heat treatment after accelerated ions have been implanted at depths of a few hundreds of nanometers. For example, lead chalcogenide quantum dots are synthesized by sequential implantation of Pb and one of the chalcogen species into pure silica [23], followed by annealing at 850–900 °C for one to eight hours to reach a maximum concentration of about 0.3 at. %.

5.3.2 New Strategies

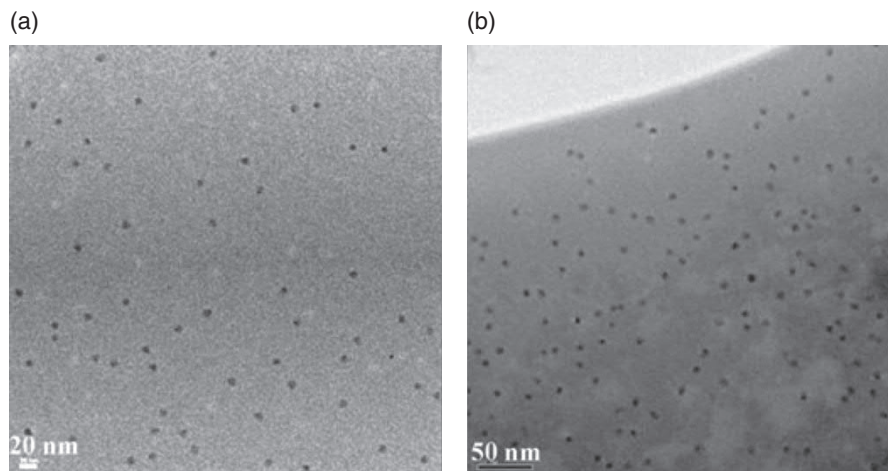
In optoelectronic applications, it is important to control not only the size but also the distribution of quantum dots. Rare-earth ions are thus widely used as nucleating agents. The number of PbS quantum dots is, for instance, 251 and 1025 per μm^2 as measured from a 2-D TEM micrograph in glasses containing 0 and 0.2 mol % Er₂O₃, respectively, after annealing at 500 °C for 20 hours (Figure 17) [22]. Addition of rare-earth ions causes both the absorption and photoluminescence peaks of PbS to shift to the shorter wavelengths, indicating that the size of PbS quantum dots then decreases.

A similar effect is achieved with Ag nanoparticles, which in addition provide an alternative method to form

quantum dots at a depth of only tens of microns below the glass surface by diffusion of Ag⁺ ions from AgNO₃ melt or a silver paste. The specimens are then heated first near 350 °C to precipitate Ag nanoparticles and then at about 420 °C to precipitate quantum dots only in the Ag⁺-affected regions. The amount of Ag migration into the glasses as well as the size of PbS dots can be controlled through adjustment of the temperature and duration of the annealing. The method is particularly effective for site-selective formation of lead chalcogenide quantum dots in glasses for planar or waveguide photonic devices.

Femtosecond laser irradiation is another useful method for ensuring ion diffusion through local accumulation of heat. By a Soret effect, the concentrations of network formers increase in the irradiated region as a result of out-diffusion of the small network modifiers. Upon femtosecond laser irradiation, cadmium/lead and chalcogenide species thus redistribute and precipitate as quantum dots with a controlled spatial distribution. For example, a laser with a pulse width of 184 fs can be used at a repetition rate of 1 kHz and a pulse energy of 247 μJ to irradiate the glass specimen and form 50 μm underneath its surface a 2-D square (2×2 mm) pattern consisting of 1600 spots separated by 50 μm . After irradiation of each spot by 200 pulses, the glass specimen heated at 420 °C for 20 hours

Figure 17 Evaluation from TEM image analyses of the number density of PbS quantum dots in borosilicate glass annealed at 500 °C for 20 hours [22]. (a) Glass without Er_2O_3 doping. (b) Glass doped with 0.2 mol % of Er_2O_3 .



has precipitated large, dense PbS quantum dots and shows strong color changes in the irradiated compared with the non-irradiated regions. A strong photoluminescence peaking at ~ 1200 nm is indeed observed in the irradiated region, whereas only a weak emission band occurs at ~ 1100 nm elsewhere.

5.4 Potential Applications

Chalcogenide quantum dots have a short relaxation time made up of two components, a fast in the tens of picosecond range and a slow one in nanoseconds. Therefore, glasses containing dots with different sizes have been used as saturable absorbers in a wide range of wavelength (e.g. CdS/CdSe/CdTe quantum dots, 510–850 nm; PbS/PbSe, 1000–2000 nm) under different operating laser conditions. A detailed study of the use of such saturable absorbers for passively mode-locked and Q-switched solid-state lasers can be found in [24].

Glasses containing chalcogenide quantum dots can also be used as active optical components such as LED color converters (Chapter 6.9) and fiber-optic amplifiers utilizing their tunable photoluminescence from the visible to the infrared range. A white LED color converter with CdSe quantum dot-doped silicate glass has, for instance, been successfully fabricated [25]: the heat-treatment conditions have been optimized in terms of the size of quantum dots through which the white light can be observed when the doped glasses are mounted on a 450 nm blue LED chip. One can then adjust the CIE (Commission Internationale de l'éclairage) color coordination of the device by varying the size of CdSe quantum dots through controlling the heat-treatment conditions (Figure 18). The color coordination thus moves from blue to red as the annealing duration increases up to 15 hours. Compared with the phosphor-embedded organic resins

commercially used, these glasses thus provide thermally and chemically more stable matrices, thereby eliminating the problem of resin degradation (Chapter 6.9).

Glasses containing lead chalcogenide also have the potential to become universal fiber-optic amplifiers in the telecommunication network where rare-earth doped amplifiers are most successful. As determined by the electronic structures of rare-earth ions, however, their amplification windows are narrower than 100 nm. By tuning the size of lead chalcogenide quantum dots, one can in contrast cover the whole 1260–1675 nm optical telecommunication window. Optical amplification at 1330 and 1550 nm also obtains in bulk glasses containing PbS quantum dots. In practice, a problem met during fiber drawing is uncontrollable growth of the dots, but it has been solved by a melt-extraction method with which the transparent precursor glass fiber is made [26]. In this way, near-infrared emission has been obtained from heat-treated fibers doped with PbS.

6 Perspectives

Interestingly, the coloring effects in stained glass of Cd and Se tiny particles became known empirically in late nineteenth-century Art Nouveau, i.e. well before the discovery of quantum dots [27]. Since then the interest has shifted to the intensity, lifetime, and other radiative properties of light emission from rare-earth ions in chalcogenide and chalcohalide glasses, which have a definite potential for amplifiers in fiber-optic communications. For example, the lifetime and intensity of the 1.31 μm emission level (${}^6\text{F}_{11/2}$ – ${}^6\text{H}_{9/2}$) in Dy^{3+} are significantly higher in chalcogenide and chalcohalides than in other glasses. Rare-earth ions in sulfide glasses are mainly surrounded by approximately seven S ions whereas they were coordinated by $\sim$ six Br ions in chalcohalide glasses

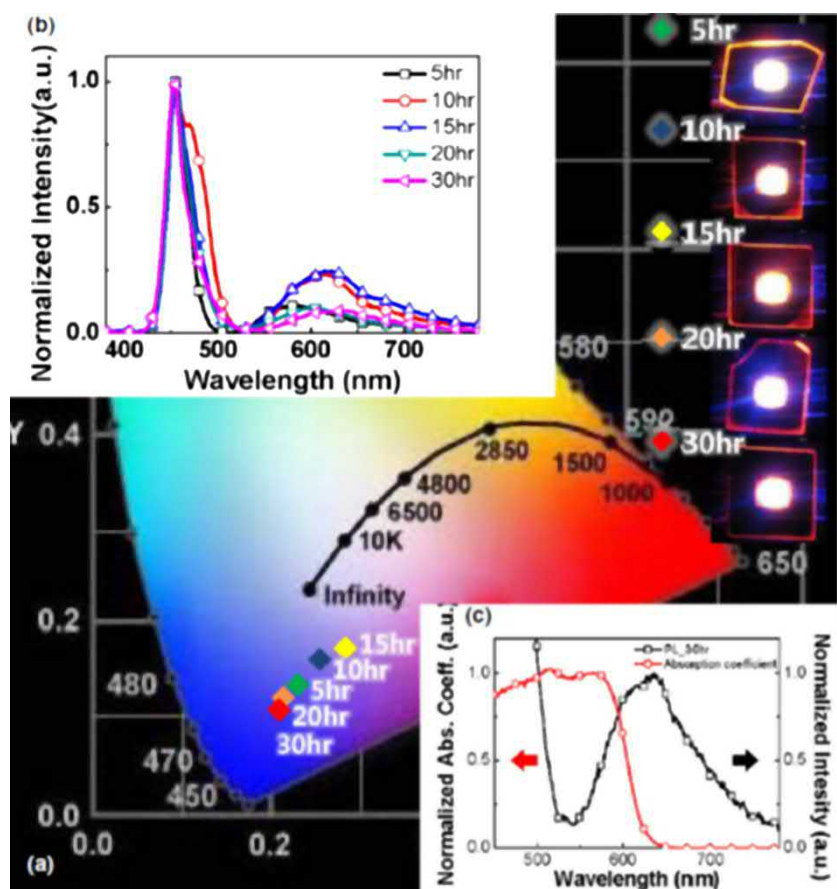


Figure 18 Effect of the size of CdSe quantum dots in silicate glass on LED color converters [25]. (a) CIE color coordination after annealing at 520 °C for varying durations; actual photographs of the LEDs displayed on the right-hand side. (b) Electroluminescence spectra of the LEDs. (c) Photoluminescence spectrum and overlap between the absorption and emission spectra of the glass annealed for 30 hours.

containing CsBr. Hence, they experience a reduced electron–phonon coupling that enhances emission properties.

Thanks to their low phonon energy and high transparency, chalcogenide glasses are also highly promising materials for mid-infrared gain media when doped with rare-earth ions. Characteristic emission band at 3000 and ~4300 nm and a broad feature between 3500 and 5500 nm are observed from Dy^{3+} and Pr^{3+} doped Ge–Ga–Sb–Se glasses, respectively. Codopants such as Pr^{3+} , Ho^{3+} , and Tb^{3+} further improve the emission via efficient energy transfer to the active ion. The Tm^{3+} ion is also beneficial to Pr^{3+} ion upon pumping at 2005 nm to enhance the mid-infrared emission due to the $^3\text{H}_5 \rightarrow ^3\text{H}_4$ transition. Likewise, Dy^{3+} - and Pr^{3+} -doped selenide optical fibers produced display mid-infrared emission promising for laser materials.

Glasses containing chalcogenide quantum dots have been extensively investigated over the past three decades. Efforts have focused on the quantum size effect, size control, absorption, and photoluminescence properties and on the development of new applications. The main challenge to overcome includes improvements of currently low luminescence efficiencies resulting from defects at the interface of the quantum dots with the glass matrix.

These surface defects give rise to nonradiative recombination or trap emission and, thus, reduce direct recombination from electrons and holes. It is difficult, although not impossible, to passivate the surface of quantum dots because they are isolated by the glass matrix from the beginning of the nucleation stage. Innovative methods need to be developed to modify these surface defects if one were to realize high-efficiency optical devices. Another challenge is to avoid the secondary growth of quantum dots during the fiber-drawing process. When drawing PbS-doped glass fiber from the preform, such a secondary growth occurs at elevated temperatures. Although this growth can be controlled with melt-extraction methods, it can be done only to bare fibers. For practical applications, the drawing process must thus be modified so as to produce glass fibers doped with quantum dots that have an outer cladding layer.

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6.7

Modification Technologies of Glass Surfaces

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1 Introduction

That surfaces have special properties was made clear when Newton [1, 2] reported in 1686 that two flat glass plates pressed together could hardly be separated and that some liquid inserted between the plates made separation still more difficult. The origin of such phenomena long remained enigmatic even though it had to be related to the differing arrangement of atoms or molecules at the surface and in the bulk of a solid. The changes in the physical and chemical properties of surfaces are not limited to their topmost monolayer, however, but to a more or less extended transition region. Many investigations of these properties have been undertaken but only a few monographs concerning the properties of glass surfaces were available as late as the 1960s [3, 4].

Early experiments concentrated on the attractive forces investigated by Newton. Macroscopic degradation such as corrosion, abrasion, and wear had been observed on the surface or in near-surface regions for different glasses but a microscopic understanding of such effects was limited because surface-sensitive analytical tools were not available. It was nonetheless known that various factors influence the nature of a glass surface and that, even for the same material, different forming methods produce different surface properties.

Chemists investigated the interactions between the surfaces of solids and liquids or gaseous ambient surrounding it. For example, the various forces involved in physisorption, chemisorption, and chemical binding had been measured, and their origin explained. But physicists were

not interested in contamination effects. They considered the structure and prevailing binding forces in solid-state materials ideal for research but systematic investigations were hampered by adsorbed foreign layers of unknown compositions. The situation changed in the 1980s when the development of ultrahigh vacuum (UHV) technology allowed fresh solid-state surfaces to remain clean for several hours. This advance led to a new research area, surface physics, and to an improved understanding of various phenomena at glass surfaces. These were, for instance, reviewed during a conference entitled *The Surface: A Bug in New and Old Glasses* organized in 2000 in Venice by P. Mazzoldi in cooperation with Technical Committees of the International Commission on Glass (Chapter 9.11).

Today, many issues pertaining to technical materials are accepted as surface problems whereas improved surface properties are themselves seen as offering many opportunities for glass applications. Therefore, considerable research has been invested in recent decades in studying surfaces and developing technologies for glass-surface treatments whose success also depends on understanding better simple age-old procedures like grinding, polishing, structuring, and cleaning.

Surfaces are described in many ways. Mathematicians may see them as two-dimensional topological manifolds whereas solid-state physicists may refer to the broken symmetries of the bulk. But such definitions limit the complexity to one view and ignore the physical and chemical phenomena that occur particularly at solid-liquid and solid-gas interfaces. A real glass surface can be described macroscopically by an abrupt change between solid glass (defined by its chemical composition and production history) and the surrounding medium (which influences the history). Microscopically, however, there is no abrupt boundary but different transitional zones with specific compositions and structures between

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the glass and its environment, which depend on many parameters. Chemisorbed water, for instance, dominates the chemistry of silicate glasses from the bulk to the glass surface through the near surface region. In multicomponent glass systems, this feature leads to in-depth hydration, surface layer formation, and corrosion (Chapters 5.11 and 5.12). Beginning with manufacture, slow alteration of the glass surface is a universal and never-ceasing phenomenon. These changes depend on the interactions with the environment, time of exposure, temperature, and other conditions. These natural responses of a surface to the manifold interactions with the different contacting media are the basis for very powerful surface technologies, which can be used to manipulate the properties of the glass.

Most physical and chemical properties of glasses are influenced by special surface treatments so that specific functionalities for various applications can be created. For example, the mechanical properties of glass are of fundamental importance. Because surface defects cause the practical strength to be far below its theoretical value (Chapters 3.11 and 3.12), their effects can be minimized by the deposition of thin films or by compressive stresses resulting from chemical modifications of surface layers by ion exchange.

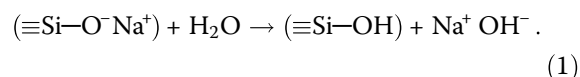
Many surface technologies are available (Figure 1). They can be categorized as (i) removal of material from the surface by mechanical, optical, or thermal treatment; (ii) exchange of species from the glass with the environment by chemical or physical driving forces, for instance, by diffusion; (iii) addition of material by different coating processes (Chapter 6.8). The choice depends on the requirements of the applications. Since the market value of glass products will increasingly depend on their surface properties, even more technologies are under development. This chapter thus describes the fundamentals of the underlying processes and their applicability. Surface properties are first determined by the glass-forming

process because pressing, blowing, drawing, or floating yield characteristic properties that differ for the same bulk composition. At the hot end of production, additional processes can then modify the surface, for example, to facilitate handling of the virgin products or to reduce corrosion as will be exemplified here with dealkalization and flame polishing. The influence of glass forming and hot-end processing on surface quality will thus be discussed. Relevant technologies will also be explained, including surface cleaning, polishing, structuring, ion exchange, and thermal treatment and examples of their use for traditional products and more advanced applications will be presented.

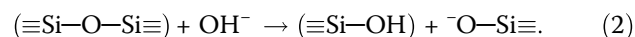
2 Hot-End Processes in Glass Production

2.1 Dealkalization

When glass is in contact with water, aqueous solutions, or humidity, its morphology and composition change in the surface region as described by two kinds of corrosion reactions (Chapter 5.11, [5]). The first is an ion-exchange reaction (leaching) between network-modifying ions such as Na^+ in the glass and H^+ ions in water resulting in the formation of Si-OH groups, the release of network modifiers, an enrichment in hydroxide ions and, thus, a pH increase:



Once the pH reaches 9 or more, hydrolysis begins to generate silanol and non-bridging oxygens:



As discussed in Chapter 5.11, these reactions can take place right after production during transportation,

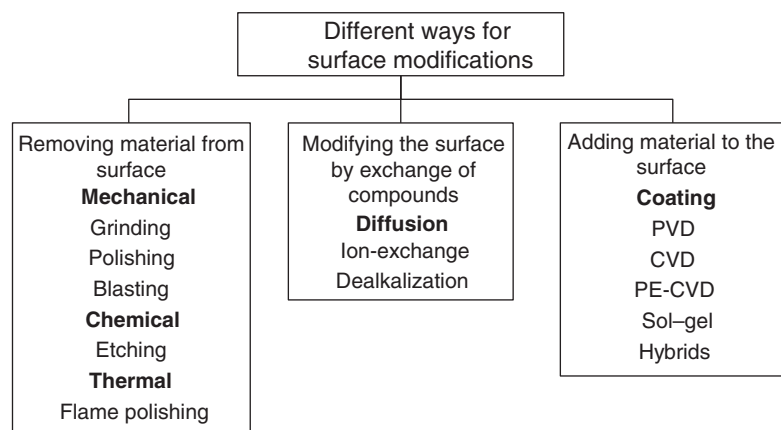
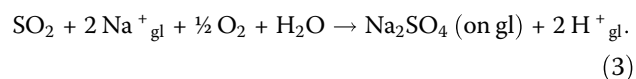
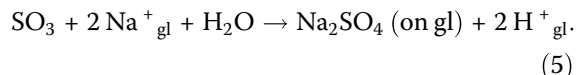
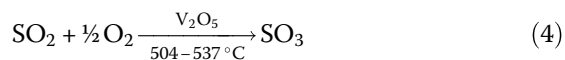


Figure 1 Basic processes of glass-surface technology.

storage, and even final use if the glass temperature falls below the dew point of the atmosphere [6], in which case the chemical and physical properties of the surface differ from those of the bulk [7]. The various ways available to prevent the problem or limit its consequences have also been described in Chapter 5.11. Here, we will thus restrict to the problems raised by diffusion of mobile Na^+ ions toward the surface that cause defects such as fracture and cavities and affect the chemical and mechanical reliability of coatings through poor adhesion, phase changes, film delamination, and optical deterioration [8]. A common way to reduce corrosion is the century-old dealkalization process whereby a thin surface layer depleted in sodium is created through reaction with SO_2 gas in the presence of water [9, 10]:



The rate of this exchange reaction between Na^+ ions in the glass and hydrogen ions is limited by the diffusion of Na^+ ions to the surface where a film of water-soluble Na_2SO_4 crystals is deposited. This rate is increased if the mixture is passed over a vanadium pentoxide (V_2O_5) catalyst at a temperature high enough to oxidize SO_2 into SO_3 before contact with the glass surface [11]:

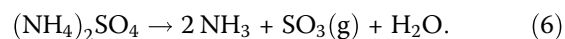


For a typical soda lime silica (SLS) float glass, the Na depletion is clearly observed in X-ray photoelectron spectroscopy (XPS) down to a depth greater than 80 nm, which compares with the 15–25 nm found for the untreated glass [12].

In the float process, dealkalization on the atmosphere and tin sides of the sheet is performed above 500°C during annealing and at the tin bath exit near 600°C , respectively. More Na is in fact eliminated on the former than on the latter side where the presence of Sn reduces the diffusivity of the mobile Na^+ ions. On the other hand, dealkalization of the tin side improves not only corrosion resistance but also surface quality because the deposited Na_2SO_4 film acts as a lubricant to protect the glass surface and heal surface defects, microcracks, or scratches created by the contact with the rollers. Complications may arise, however, and, for instance, result in local defects because the deposition of the Na_2SO_4 film depends on parameters like water content, SO_2 concentration, and temperature so that metastable

forms of Na_2SO_4 can be generated under unfavorable operating conditions [13].

In the glass-container manufacturing process, dealkalization is applied at temperatures above 500°C to achieve a higher hydrolytic resistance of the interior surface. The resistance is measured by titration with an acid solution according to the international standard ISO 4802-1 (Chapter 5.1). There are other dealkalization methods. When solid $(\text{NH}_4)_2\text{SO}_4$ or aqueous solutions are introduced within the container after forming, they decompose above 500°C in the annealing lehr to produce the SO_3 gas needed for the dealkalization reaction [14]:



The method is ecologically safe since unreacted components do not escape to the atmosphere. Rather, they react with each other to form the original salt in the container, which can later be rinsed away. The drawback of the process is fracture of glass because solid $(\text{NH}_4)_2\text{SO}_4$ or aqueous solutions may cause the glass to supercool and break it.

2.2 Flame Polishing

Surface quality is one of the most important constraints to be respected by tableware and container manufacturers. For pieces produced by press technology, flame polishing is most widely used to improve it. By impinging on the surface and remelting a thin layer (Figure 2), flames allow specific regions to be heated precisely for eliminating surface defects like burrs, sharp edges, stains, and cracks, minimizing surface roughness and enhancing brilliance. The improvement is obvious in optical profilometry images of glass surfaces (Figure 3). Additional advantages of the method are to eliminate the usage of either mechanical processing or acid polishing with hazardous chemicals like HF and to make automatically produced glassware resemble handmade pieces.



Figure 2 Flame polishing in production.

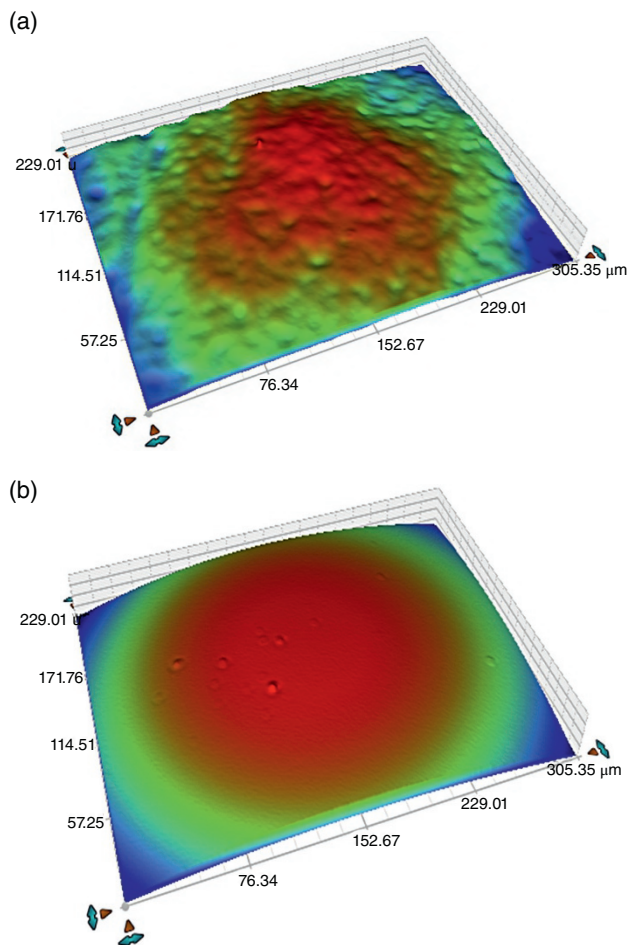


Figure 3 Optical profilometry images of glassware surface that is formed by the press process: comparison between the initial rough state (a) and the smooth and almost defect-free state after flame polishing (b) [15].

Process parameters for flame polishing are the gas flow, heat transfer rates, working distance between burners and glass surface, flame shapes, gas ratios, and pre- or post-mixing of gases. If these parameters are improperly chosen, surface defects can form on some parts of the surface, which may get corroded after a certain number of cycles in a dishwasher (Figure 4). This corrosion has been assigned to alkali enrichment of the surface upon flame polishing and subsequent hole formation that manifests itself as partial surface clouding after dishwashing [16]. The phenomenon has been more precisely described with the help of atomic force microscopy (AFM) and other high-resolution analytical techniques [17]. In remelted areas, alkali and alkaline earth ions may evaporate to condense on colder regions (Figure 5). In the form of holes (Figure 6), preferential dissolution of these areas in the dishwashing environment then causes the observed clouding (i.e. light scattering).



Figure 4 Glassware partially corroded (in the middle part) during dishwashing as indicated by the scattering of light caused by the presence of numerous holes.

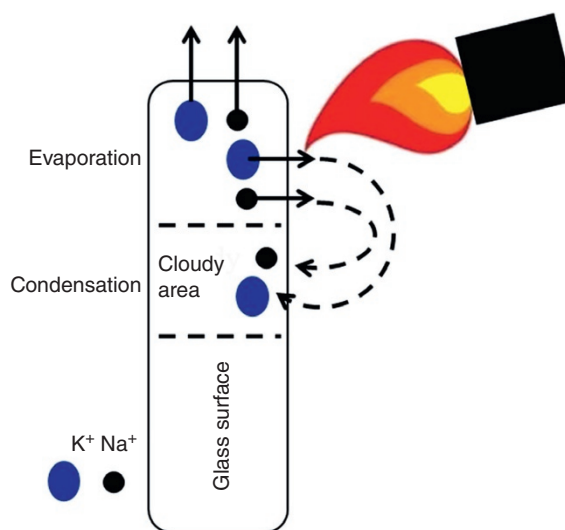


Figure 5 Sketch of the flame-polishing process: evaporation and condensation regions.

3 Cleaning

Glass surfaces can be contaminated by inorganic or organic matter found as particles or as films and brought by gases, liquids, or solids present in the atmosphere and other media. Not only is the number of sources nearly unlimited but also the bulk glass is often contributing to the contamination by diffusion. Different phenomena like adsorption, chemical reactions, leaching and drying procedures, mechanical treatment, as well as diffusion and segregation processes can give rise to surface contaminants of various compositions. Cleaning of glass surfaces thus is a serious issue. At the atomic scale, the clean

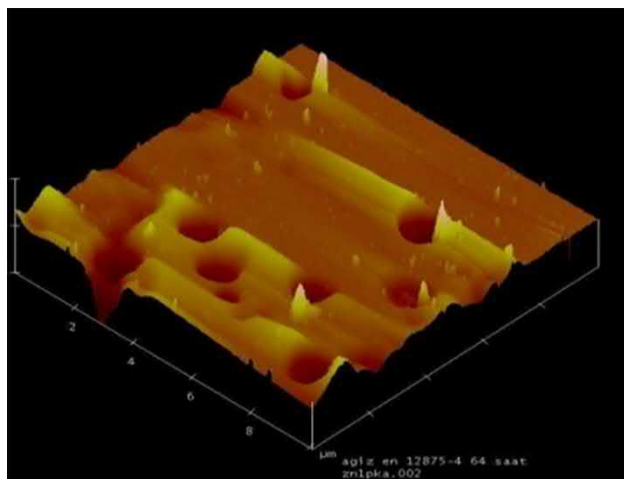


Figure 6 Holes about 1 μm in diameter formed after dishwashing as seen in height-mode AFM images of a glass surface 3–4 mm away from a flame-treated area. Scratches and contamination fragments only observed before flame polishing.

surfaces needed for scientific purposes, for example, to study interaction mechanisms, can only be obtained under an UHV. Because these conditions are not relevant industrially, we will deal here with the *technically clean* surfaces required not only for tableware, windows, smart phones, or eye glasses but especially for surfaces that must be coated with thin films in a variety of scientific or technical applications [18]. Because no universal cleaning methods exists, however, all are tailored to specific glass surfaces and a combination of them is often required to achieve the cleanliness required by the application of interest.

Different techniques are thus used depending on the contaminant, glass type, and dimension of the pieces. Usual methods involve scrubbing or polishing the surface in combination with various cleaning fluids. Traditionally a pre-cleaning operation consists in rubbing the surface to remove any dirt as done for eye glasses, lens, or mirrors with a tissue saturated with an appropriate fluid. The type of glass and the nature of the contaminants determine which solvent is to be applied in the liquid or vapor state and at which temperature. These solvents include deionized water, aqueous solutions of detergents, diluted acids or bases at various concentrations, and nonaqueous solvents such as alcohols, chlorinated or fluorinated hydrocarbons.

A simple and common technique is immersion or dip cleaning whereby the wetted glass pieces are removed from the solvent tank after a short time and dried. For certain glasses, chemical reactions are also exploited with various liquids under a wide range of pH values. Most acids are used warm between 40 and 80 $^{\circ}\text{C}$. Silica is not readily dissolved by acids, except by hydrofluoric acid.

Higher temperatures may aid silica dissolution so that a fresh surface is created on the glass. Acid cleaning cannot be used for all glass types.

As used since about 1950, ultrasonic (US) cleaning is particularly effective to remove in a few seconds or a few minutes strongly bonded contaminants such as pitch and polishing-agent residues from optically worked glass. Cleaning is performed in a tank containing the appropriate solvent usually kept at about 40–65 $^{\circ}\text{C}$ and equipped with transducers that convert an oscillating electrical input into ultrasound waves of 20–400 kHz frequencies. The compression waves propagating in the solvent create microscopic “voids” or “partial vacuum bubbles” (cavitations), which remove surface dirt and contaminant by collapsing onto them with a high-energy density. The higher the frequency, the smaller the nodes between the cavitation points and the more intricate are the structures that can be cleared. In addition, one can of course increase the cleaning efficiency by increasing the power input and cavitation density.

Many thin-films are deposited under vacuum. Procedures have thus been developed to clean surfaces prior to coating under the same conditions. Vacuum does cause evaporation of volatile impurities, but the process depends on the remaining pressure, duration, substrate temperature, and type of contaminant. Glass surfaces are traditionally heated at 100–350 $^{\circ}\text{C}$ for 10–30 minutes before coating to remove part of the water and various hydrocarbon molecules adsorbed. Atomically clean surfaces require an UHV and temperatures higher than 450 $^{\circ}\text{C}$ so that other techniques have been developed to import more energy onto glass surfaces. For instance, an ozone-producing UV source rapidly decomposes hydrocarbons on properly pre-cleaned surfaces. The highly reactive oxygens produced by ozone actually react with the free radicals produced by the dissociation of the contaminant to form volatile molecules like H_2O , CO , and N_2 .

Electrical-discharge cleaning at a reduced pressure immediately prior to film deposition is also widely used. With plasma cleaning, impurities and contaminants are removed by reaction with excited atoms and ions formed at typical kHz to MHz voltage, which emit a characteristic light-glow when they return to their electronic ground state. Be they atoms, molecules, ions, electrons, free radicals, and vacuum UV photons, the various activated species present in the plasma interact with any surface with which they are in contact.

Plasmas produced from oxygen gas are efficient and environmentally safe for critical cleaning. The various oxygen species created in the plasma (e.g. O_2^+ , O_2^- , O_3 , O , O^+ , O^- , ionized ozone, excited oxygen, and free electrons) assist cleaning. They react with organic contaminants to form H_2O , CO , and CO_2 , and lower the

molecular weight of the hydrocarbons. While these activated oxygens react with organic contaminants to form volatile compounds, the glass surface is chemically modified by oxygen addition and loss of components such as alkalis.

In addition, the vacuum UV energy is effective in breaking most organic surface-contaminant bonds, dissociating high-molecular weight contaminants and creating volatile compounds. The contributions of the individual processes depend on various electrical and geometrical parameters and discharge conditions. The most important parameters in glow-discharge cleaning are the applied voltage, the current density, type of gas and gas pressure, duration of treatment, type of glass to be cleaned, and shape and arrangement of the electrodes. Owing to particle bombardment and surface interactions of ions and electrons, the transfer of energy to the substrate causes its temperature to increase up to 200 °C, which favor further the desorption of adsorbed water and some organic contaminants.

Substrate cleaning in high vacuum by ion bombardment generated in special ion sources is rarely used in industry. Ion-beam technologies offer interesting opportunities, however, not only for cleaning but also for the polishing and machining of optical surfaces, for structuring, and for modifying the optical constants of the glass surface in regions that may be of interest for making micro-optics and integrated optical devices.

In summary, surface cleaning is performed by various methods, such as washing with solvents, heating, UV, and plasma treatment. Each has its specific domain of applications. Solvent cleaning has the greatest range of utility but is inadequate in many cases, particularly when the solvents themselves are contaminants. Heating is useful only up to a maximum temperature so that plasma treatment represents a valuable method when contaminants are so strongly bonded that higher temperature would be needed to eliminate them because the plasma energy can be much higher than achieved thermally without damaging surfaces, thanks to its low flux.

4 Strengthening

4.1 Ion Exchange Processes

Two common technologies to improve mechanical properties rely on the stress generated in the glass surface region by ion exchange and thermal treatment. Referring to Chapter 3.12 for detailed presentations, it will suffice here to recall that, by dipping a preheated float glass sheet into a tank of molten KNO_3 below the strain point for several hours, one substitutes small

Na^+ ions by larger K^+ ions and creates in this way compressive stresses near the surface large enough to increase the glass strength by a factor of 3–5. Although discovered many years ago [19], the process failed to penetrate large markets until the advent of chemically strengthened flat aluminosilicate glasses such as Corning® Gorilla® Glass, Schott Xensation™, or Asahi Dragontrail™, which have become high-value keystone components in displays and handheld electronic devices (Chapter 6.10), solar cell covers (Chapter 9.4), and, increasingly, automotive glazing (Chapter 9.2) in addition to gradient index lenses and waveguides. For reasons of cost, throughput, and specific technical challenges, however, today's applications are still limited to small-area glasses although the process has the advantage of being applicable to curved or thin glass articles.

4.2 Thermal Tempering

In glass production, temperature plays a crucial role not only upon melting but also on cooling and during post-treatment procedures. The most commonly used process for thermal tempering requires uniform heating to approximately 600–650 °C followed by a rapid cooling by air blown uniformly onto both surfaces simultaneously. Quenching creates near the surface a high compression over approximately 20% of the glass thickness whereas the central core finds itself under tension. Under uniform loading, heat-treated glass is stronger than annealed glass of the same size and thickness. Depending on the degree of residual surface compression or edge compression, heat-treated glass are said to be heat-strengthened or fully tempered. The higher compression levels can create products that are generally stronger than annealed glass and twice as strong as heat-strengthened glass of the same thickness and type. As the compression levels increase, the size of the fragments of broken glass tends to become smaller.

With the exception of strength and breakage characteristics, these glasses retain the normal properties of annealed glass, including chemical resistance, hardness, expansion, and optical characteristics. Heat-treated and tempered glasses have been produced for the architectural market for more than 30 years, being now surpassed in volume only by annealed glass. Today, products are available for architectural (Chapter 9.1) as well as for residential and for automotive applications (Chapter 9.2). They are also called *safety* glasses since tempered pieces break into small fragments, which are less of a hazard than the large and sharp pieces resulting from a broken lite of annealed glass.

5 Modification of the Surface Topography

5.1 Process and Surface Topography

The topography of a glass surface strongly influences features ranging from light scattering to chemical reactivity. When thin films are deposited, their adherence and microstructure in addition depends on their interactions with the surface and its topography, which is generally not perfect and homogeneous at a microscopic scale. Depending on the length scale, it is useful to distinguish between *flatness* in the cm range or more, *waviness* at the scale of the wavelength of light, and *roughness* in the nm range.

The topography is determined by both the production process and glass composition. In general, all glasses shaped by pressing, drawing, or rolling show characteristic marks that often replicate the surface of the tools with which they were in contact. Thanks to the preservation of the originally smooth interface of the liquid, such features are not present in flame-polished surfaces produced by usual blowing techniques and the float process. Likewise, a low surface roughness in the nm range is achieved by other forming processes when there is no direct contact with the soft molten phase. For example, most drawn glasses have smooth surfaces with occasional surface irregularities of approximately 100 nm in height. But drawn borosilicate glass tends to be wavy because of its relatively high drawing temperature and short working range.

5.2 Grinding and Polishing

For simply shaped surface contours, hot pressing and molding of glass are used without further surface finishing operations to produce, for example, mirror substrates for various small projector lamps, signal lamps, or automobile reflectors. More complex and accurate surface shapes of high-quality products, like glasses for optics, electronics, space technology, and biomedical applications, are produced in curve-generating machines by milling and lapping operations. Different operational steps are then required with increasingly finer grinding grains to achieve a finish suitable for starting the polishing process.

The grinding process is dominated by physical effort. Small glass fragments are removed when they break out under the action of loose or bound abrasive grains (silicon carbide, electro corundum, or diamond) tied to iron or brass discs, which are harder than the glass itself and have a size that determines the particle size broken out upon grinding. The combined effect of the load of the abrasive particles and the additional tensile stress in the surface that results from their frictional pull cause breaking and flaw formation. The pressure of the shaping tool

on the surface and the relative speed between tool and glass are directly proportional to the weight removed. Water is used both as a cooling medium and an agent distributing evenly the grinding grains.

After grinding, polishing serves to produce homogeneous and optically highly transparent surfaces with a low roughness, be they extremely flat, spherical, aspherical, or of a complex shape. Metal oxides (ZrO_2 , Fe_2O_3 , CeO_2 , AlO_3 , etc.) on cloth or pitch polishers are applied to smoothen the surface in the presence of water. Polishing theories are roughly classified into three groups [3]: (i) in the *wear* theory, polishing is an extension of grinding involving the mechanical removal of asperities; (ii) in the *flow* theory, asperities flow plastically into surface cavities under the pressure exerted or upon frictional heating; (iii) in the *chemical* theory, the asperities are removed by transformation into compounds produced in chemical reactions with the polishing agents that can then be easily removed mechanically. Combining such physical and chemical effects, the main parameters affecting the polishing process are not only the glass type and the surface state after grinding but also its speed, pressure, and kind of materials and compounds used.

There are various ways to polish glass surfaces. In technical applications, polishing requires at least two steps. First, the ground gray surface is smoothed by the action of the oxide/water slurry and a silica gel is produced as a reaction product of glass and the polishing agents, which smears and glazes the smoothed surface areas and fills the remaining cavities. The created surfaces are rather smooth but have high waviness. In the second step, the conditions are adjusted to favor smearing and enhance polishing. The latter is important to remove the last remaining cavities. At the end of the process, the remaining polished layer consists mainly of silica gel and, therefore, differs appreciably from the bulk glass.

For high-quality optical glass surfaces, ion figuring is applied. This is a complementary, non-contact technology to avoid or eliminate problems associated with traditional contact polishing. The process is based on bombardment by particles of an inert gas, which results in soft sputtering of the substrate material. The technique is an excellent tool for contour corrections or for ablating the water-rich polishing layer. It does not improve the surface smoothness, however, and can expose subsurface damage on less carefully, traditionally polished samples.

6 Structuring and Texturing

More and more modern applications need specific structures in the surface region. For structuring and texturing in the nm to μm range, various approaches are applied in

industry and many more are under development. Traditionally, molding or embossing techniques have been used for the fabrication of patterned surfaces based on the viscous deformation at temperatures close to the glass transition temperature T_g (Figure 7).

In the cold state, wet chemical etching with hydrofluoric acid and also sandblasting are common to obtain frosted or matted surfaces. Now, CO_2 lasers producing infrared radiation ($10.6\ \mu\text{m}$) are used to structure glass whereas laser-etching techniques combined with wet etching are being evaluated and novel atmospheric-pressure plasma-assisted laser ablations are under investigation. More sophisticated processes are also being applied to structure glass surfaces, such as electron-beam, laser interference lithography, or reactive-ion etch process with gas mixtures of CF_4 and O_2 . In particular, more advanced glass applications in which glass is used in combination with silicon, such as PVs or MEMS, created a demand on new structuring technologies.

For example, aluminum-induced texturing (AIT) is a promising and potentially low-cost method [21–23]. As indicated by a schematic process flow (Figure 8), a thin metallic Al film deposited on the glass surface is annealed at high temperatures in an inert atmosphere to initiate a redox reaction at the interface ($4\ \text{Al} + 3\ \text{SiO}_2 \rightarrow 3\ \text{Si} + 2\ \text{Al}_2\text{O}_3$). Removing the reactants by wet-chemical etching, one obtains a textured glass surface made up of c-Si clusters surrounded by Al_2O_3 crater-shaped nodules embedded into the glass, with a width and a depth of about 5 and 1 μm , respectively [24]. The surface texture depends on the nucleation conditions during annealing. With AIT (Figure 9), the total reflectance of the glass surface is 1–2% lower than that of the bare glass and has a significantly higher diffuse reflectance.

Such advanced surface structuring technologies open new application areas for glass. Complex surface decors or large-area surface structuring on architectural glass can be realized. For example, antireflective (AR) surface structures and coatings are needed for most existing optical components and optoelectronic devices, ranging from solar cells (Chapter 9.4), photo detectors, light-emitting diodes (LEDs; Chapter 6.9), and laser diodes. Photovoltaic cover glasses can contribute to the overall energy conversion efficiency of photovoltaic devices by improving the illumination of the converter. Patterned cover glass surfaces are one solution. Other solutions include prismatic microstructures, moth-eye surfaces, or sub-micrometer diffraction gratings applied to trap light by multiple reflections and to guide selectively the incoming sunlight.

High-precision surface microfabrication of optically transparent materials is crucial too, to structure the microfluidic channels used in lab-on-a-chip and micro total analysis systems ($\mu\text{-TAS}$), as well as for micro-optics

in photonics. Special micro-structured glass surfaces are needed for micro-mechanical, micro-fluidic, and micro-optical MEMS devices. Micro-lenses and micro-lens arrays are increasingly used for coupling in multi-fiber connectors, as collimators for LEDs and high-power laser bars. Micro-lens arrays are being implemented in wavefront sensors, pixel-based CCD cameras, confocal microscopy, and direct optical one-to-one imaging. Movable micro-optic elements for beam deflection and modulation in scanners and switches have also been reported.

In the R&D-pipelines are novel concepts and methods to make nanostructured glass surfaces for controlling the functionality of materials at the interface of applications in biology, medicine, and energy. These studies will have a large input on existing technologies.

7 Applications

Applications of the glass material have kept diversifying for about four millennia. In many traditional products such as containers or tableware, glass is preferred for obvious reasons but its surface is not a critical factor. Whereas markets for such commodity products are stable, most surface treatments are realized at the hot end of production line with the exception of thick-film technologies used for decoration. In other traditional uses such as glazing, the float-glass surface is modified to provide applications not imagined a few decades ago. In newer glass applications, concerning, for instance, information or energy technologies, glass has increasingly become an enabling component whose importance is ensured by special surface features. In some cases, the glass may be unrecognizable in the final product – but the product cannot be made without it.

A paradigm shift thus seems now underway because of “seismic” changes driven, for example, by environmental factors, a rapidly changing energy market, or advances in the biomedical field. In all these instances (Figure 10), new functionalities are or have already been developed [26] through either surface treatment or thin-film deposition (Chapter 6.8). In other words, the more advanced the product and the more important has become its surface. Traditionally, the glass surface has been perceived as ensuring chemical durability as exemplified by the dishwasher resistance of tableware. Visible corrosion was correlated with poor glass properties, which is why the chemical resistivity is used for classifying packaging materials. But R&D activities in very different sectors have changed this simplified view. More attention is now directed to glass surfaces. The need to improve glass strength to reduce weight, or to nanostructure glass

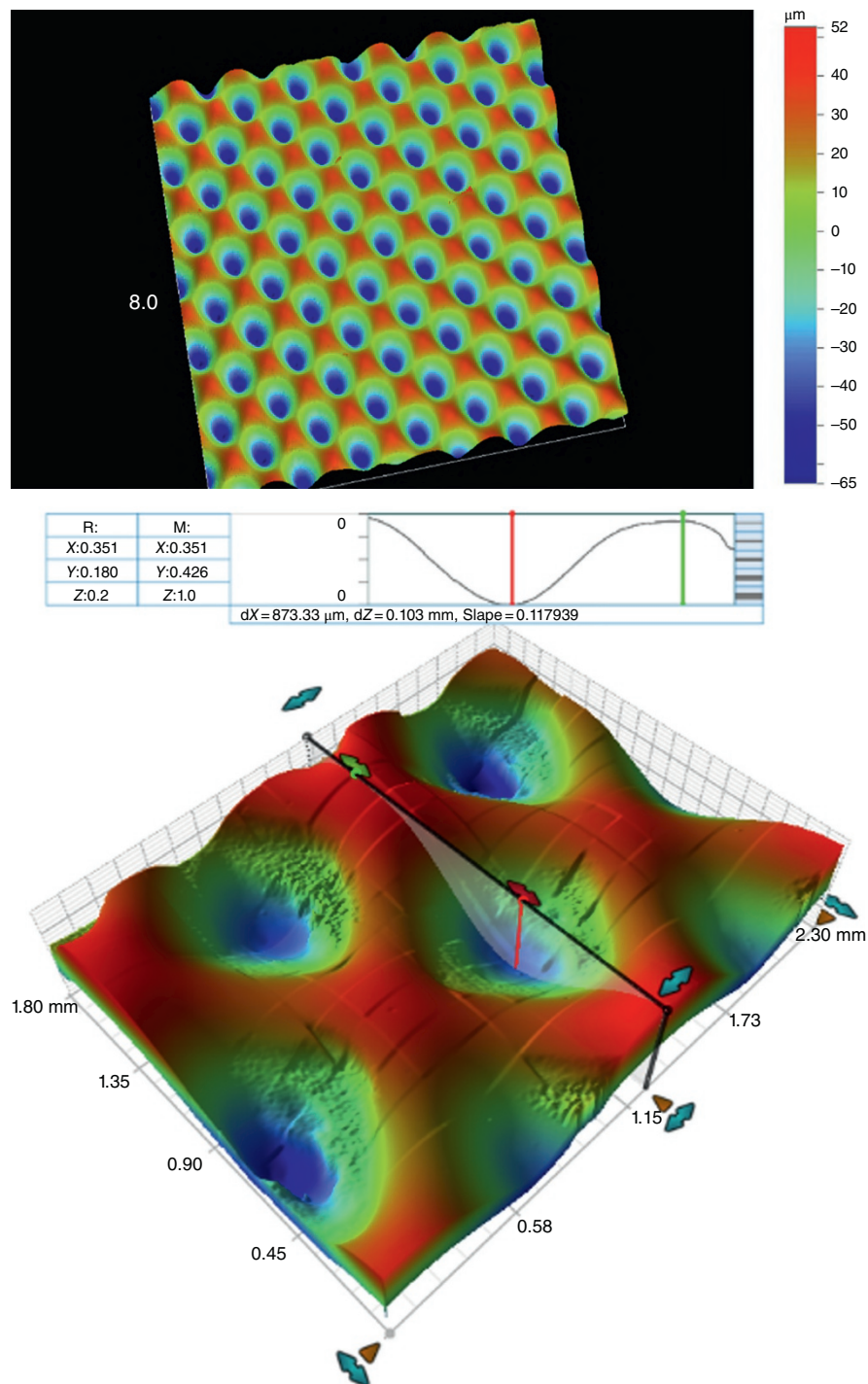


Figure 7 White-light interferometry image of a patterned glass surface [20].

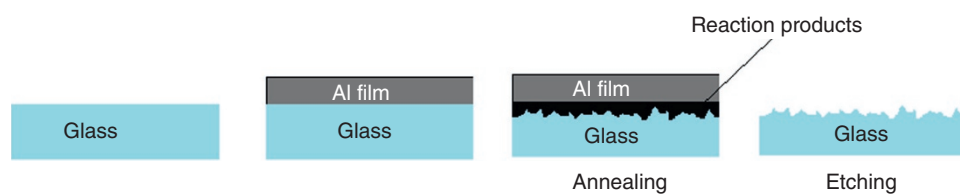


Figure 8 Process flow of the aluminum-induced texturing method.

surfaces for optoelectronic and micro-optics, and research on glass surfaces for biomedical applications have contributed to this paradigm shift.

8 Perspectives

Most advanced and future glass applications are based on very specific functionalities of the surfaces, i.e. surface technologies have become key enablers. A broad

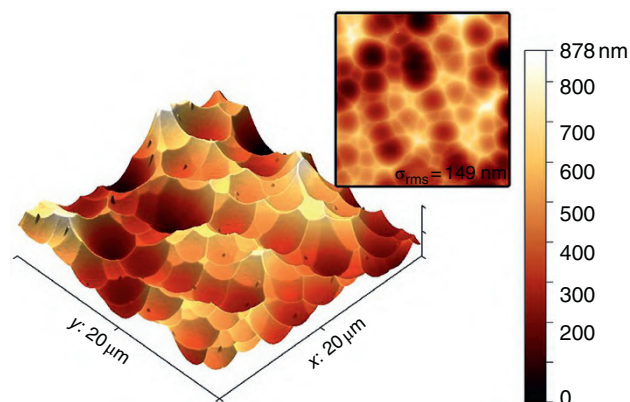


Figure 9 Atomic-force micrograph of a textured glass surface after the aluminum-induced texturing process [25].

spectrum of techniques is thus already applied and others are under development to address very different topics from roughness on the atomic scale to structured surfaces and durability in various media. Applications range from large-area glass sheets for architecture to small pieces for micro-optics. Since most, if not all, relevant glass properties ultimately depend on surface properties, these technologies will have key functions in the fabrication of glass products with novel attributes. Surface treatments (Chapters 6.8 and 8.2) will be key technologies for many future applications by providing new solutions to satisfy market demands. Existing and future applications (Figure 10) with special surface properties (and coatings) are so numerous that only a few will be mentioned in electronics, pharmaceutical packaging, and biomedicine.

Thin and ultra-thin, bendable, flexible glasses are desired for various applications, for instance, to save weight in information technology (IT) and transport systems. Displays and electronics are becoming lighter, thinner, and more flexible so that the choice of substrate continues to be critical to their overall optimization since it directly influences improvements in the design, materials, fabrication processes, and performance (Chapter 6.10). Thin and *unbreakable* glasses seem to be the “holy grail” of glass scientists in the twenty-first century. The intrinsic mechanical strength of thin glasses is already good but there remains room to reduce surface defects and the

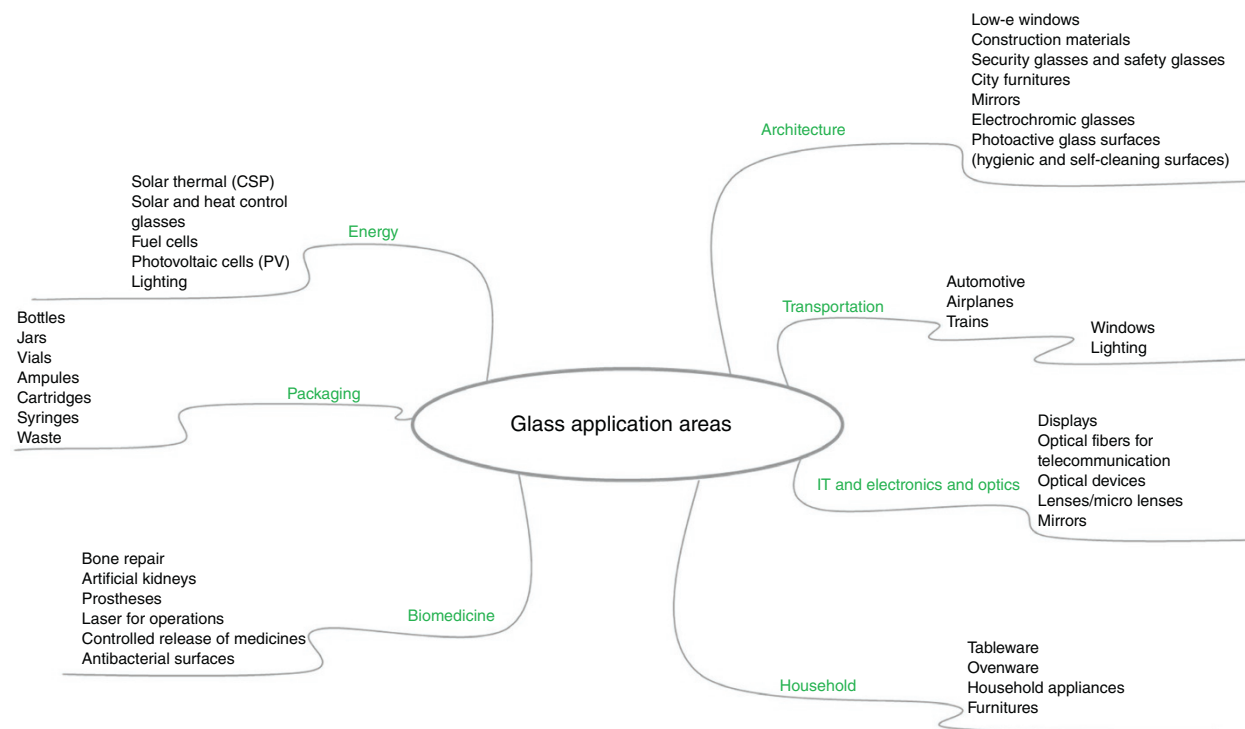


Figure 10 Application fields of modified glass surfaces: present situation and most relevant markets.

ubiquitous presence of damage caused by mechanical or thermal shock, compounded by interactions with the environment. Although glass strength is an application-dependent issue, one can enhance it in three different extrinsic ways, namely, by polishing and chemical etching to achieve a high-quality surface finish, by inducing surface compressive stresses through thermal or chemical tempering, and by coating to protect the surface.

Glass substrates enable high-quality, long-life devices, thanks to their inherent advantages such as surface quality, optical transmission, hermeticity, and thermal and dimensional stability, which are kept when the substrate thickness is reduced below 200 μm in high-performance flexible electronics. In addition, a reduction in thickness allows new device designs and high-throughput, continuous manufacturing by roll-to-roll processes (Chapter 6.10). For glass optics in high fluence and high-peak power lasers, surface quality affects dramatically the laser damage resistance so that structured glass surfaces will become more important in photonics. Future activities on nano- and micro-structured surfaces include the making of hollow-core photonic crystal fiber (PCF) from glass. New fiber lasers and sensors will be realized, optical fiber quality will improve, and nano-gratings will be formed on their surface. Other areas needing structured glass surfaces include micro-fluidics used in the lab-on-a-chip and μ -TAS.

Other examples for “new” glass surfaces come from the biopharma field where proteins, peptides, or living-cell formulations may interact with the currently available packaging more extensively than “classical” drug formulations or via different pathways. Additional topics of increasing significance arise from safety considerations (cytostatics, living cells, genetically manipulated organisms, etc.). These aspects have the consequences that future glass packaging for drugs will require surfaces with an extremely low potential for interactions with their contents and should be unbreakable (Chapter 7.7).

Many activities in cellular nanotechnology aim at making biological interfaces smarter. Engineered cell–material interfaces are generated for fundamental cellular studies, tissue engineering, and regenerative medicine. Aspects of nanostructured interfaces – nanotopographical control, dynamic behavior, and intracellular manipulation and sensing – have been investigated to understand cell function and provide new ways to control cell activity. The surfaces of bioactive glass scaffolds are also of interest, since they have the potential to match the engineering design criteria for bone regeneration when foamed to produce scaffolds that mimic cancellous bone macrostructure (Chapter 8.4). The surfaces of macropore networks are important for cell migration, bone ingrowth, and blood vessel penetration. Bioactive glasses in body fluid react to form a bone-like mineral layer on the

surface and also release soluble silica and calcium ions that stimulate cells to produce new bone.

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6.8

Thin-Film Technologies for Glass Surfaces

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1 Introduction

In the past, the special optical properties of glass have been at the roots of many technological advances. As early illustrated by the first attempts made to improve reflectivity, however, these properties had to be adjusted to make specific applications possible. As an example, the making of glass mirrors relied on the use of mercury layers, which was known by about 1369 shortly before thin amalgam films became available. As for the colors produced from light diffraction by thin films, they have fascinated observers throughout the ages; a most vivid description was made by Newton in his *Opticks* where he went far beyond a simple qualitative description of the phenomenon [1]. Later, significant enhancement of glass reflectivity was achieved with highly reflecting metal films. For instance, mirrors with silver films deposited by wet chemical processes were produced in 1835 [2, 3], well before attempts were made to deposit films on mirror surfaces by evaporation and condensation of various metals under vacuum in 1912 by Pohl and Pringsheim [4].

The first antireflection layer, for lower reflectivity applications, was deposited accidentally on glass in 1817 by von Fraunhofer [5, 6] in Germany, who recognized the unusual properties of a thin film of low refractive index when treating polished glass with concentrated sulfuric or nitric acid, but no technical application followed at that time. Much later, Strong [7] in the United States and Smakula [8] in Germany developed in the mid-1930s single-layer antireflection coatings by evaporating and condensing calcium fluoride (CaF₂) under vacuum onto glass surfaces. In 1938, Cartwright and Turner [9] suggested further suitable compounds such as magnesium fluoride

(MgF₂) and cryolite (Na₃AlF₆). Attempts to develop multilayer antireflection coatings had already been made at that time in the United States [10]. At Schott and Genossen in Germany, Geffcken [11] deposited in 1939 dielectric metal thin-films to produce a narrow-band interference filter of the Fabry–Perot type. But the practical realization of environmentally stable, complex thin-film interference systems required hard and resistant coating materials. Multilayer antireflection coatings, various interference mirror stacks, beam splitters or high- and low-pass edge filters became available in 1950 in the form of various oxide films deposited by reactive deposition. From then on thin-film materials and systems have been extensively developed alongside the conception and detailed development of both computer-aided coating design and coating production methods.

Thin films now underpin numerous applications by adding a variety of functionalities to surfaces that can be hydrophilic or hydrophobic, oleo-phobic, antifogging, slippery (lubricant), self-cleaning, easy-to-clean, anti-fingerprint, photo-catalytic, antimicrobial, antibacterial, antithrombotic or can prevent bio-adhesion, bio-films, or crusting of blood. In addition to optical properties such as transmittance, reflectance, absorbance, and color, the electrical, mechanical, or chemical properties of glass thus strongly depend on surface conditions, which is why they can be optimized by means of deposited thin films. For example, glass is known to be a good electrical insulator. For the most advanced application in information technology or in the photovoltaic sector, however, such a good electrical conductivity must be combined with a high transmittance. Thin transparent and conductive films are available today but also very thin, nearly invisible, metal bars, and electrodes have been used for decades. Likewise, the high chemical durability of glasses against acids, alkalis, staining, water, or weathering as

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assessed by durability tests (Chapter 5.1) can be improved with special coatings (Chapter 7.7). Improved scratch and abrasion resistance, corrosion protection, and an ability to act as a (gas) barrier or release system have also been engineered.

Today, coated glasses with low-emissivity (low-e) layers are the most popular products, in particular in the architectural and automotive fields. Besides those coatings, multiple layer systems on glass have been studied for more than two decades to create active or passive devices, which can change the light or heat transmission and emission properties by application of a voltage. However, only in recent years have these *smart-glass technologies* been transferred to large-volume productions and become available on the market. They have given rise to new and innovative applications and functionalities, increasing efficiency and reliability, and even decreasing costs.

This chapter thus describes the principles of manipulating glass surface properties through deposition of thin films and summarizes the most relevant deposition techniques used. It identifies the most important properties that can be modified by addition of thin films and discusses the influence of their composition, thickness, and density. The properties of technical and commercially relevant thin films and film systems on glass, such as indium-tin oxides, low-e, and antireflection coatings will be explained and several glass properties will be stressed which can be modified.

Acronyms

AR antireflective
CVD chemical vapor deposition

ITO indium-tin oxide
low-e low-emissivity
MS magnetron sputtering
NIR near infrared
OLED organic light-emitting diodes
PVD physical vapor deposition
TCO transparent conducting oxide
TCF transparent conducting film
TCM thin metallic coating

2 Deposition Techniques

The term *vapor deposition* refers to any process by which a thin film is deposited on the surface of a solid by transfer of material from the vapor (Figure 1); since the vapor is created by purely physical means, the process is called physical vapor deposition (PVD). In PVD, the production of atoms/ions/molecule species in a vapor from a solid or molten source is followed by their transfer onto the substrate in vacuum. The material may be evaporated from thermally heated sources or from sources heated by a high-energy electron beam in a chamber (thermal evaporation) or physically ejected from a solid target surface by momentum transfer of high-energy gaseous ions accelerated from a plasma (sputter deposition). Alternatively, a high-current, low-voltage arc is employed to vaporize a cathodic electrode (cathodic arc) or an anodic electrode (anodic arc) and the vaporized ions are accelerated toward a biased substrate (arc vapor deposition) or a high-power pulsed laser beam is focused to a target and the evaporated material moves in a plasma plume (pulsed laser deposition [PLD]).

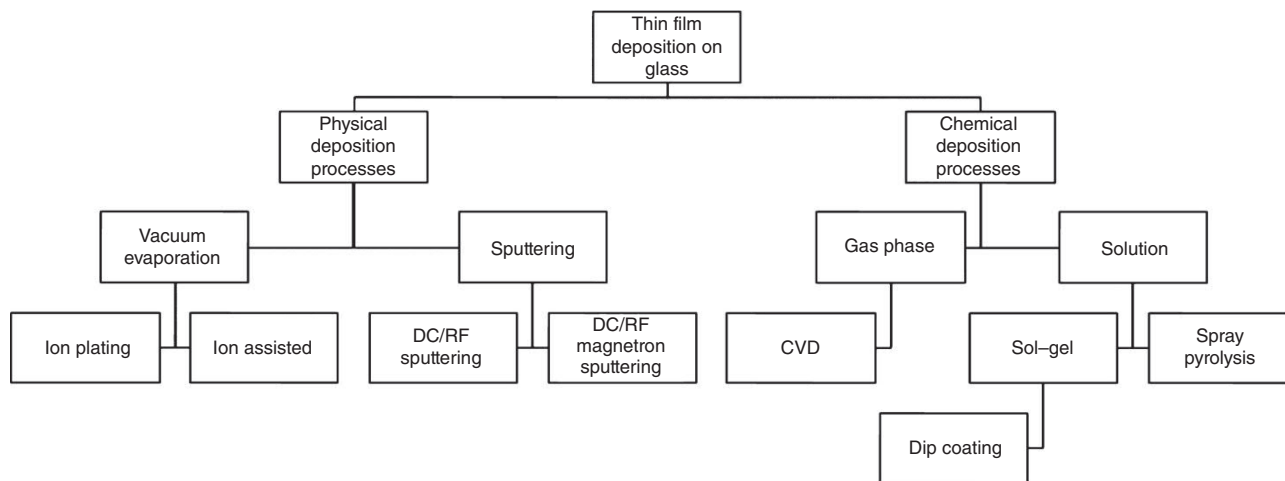


Figure 1 Overview of the most common physical and chemical processes for thin-film deposition on glass surfaces.

In chemical deposition methods, in contrast, the vapor is created through a chemical reaction either in a gas phase or in a solution. Although the former case of chemical vapor deposition (CVD) is the most important, spray pyrolysis and sol-gel methods such as dip-coating are solution-based processes that are also often used (Chapter 8.2). The three major steps in a typical thin-film CVD or PVD process are (i) the production of the appropriate atomic, molecular, or ionic species in the vapor; (ii) the transport of these species to the substrate through a vacuum; and (iii) the condensation on the glass substrate, either directly or via a chemical reaction, to form a solid deposit.

The unit vapor species impact on the glass substrate and transfer energy to it; they are adsorbed if the incident energy is not too high. These mobile adsorbed species, which are not initially in thermal equilibrium with the substrate, can interact among themselves to form bigger clusters. Depending on the deposition conditions, these thermodynamically unstable small clusters (also called nuclei, Chapter 5.4) either desorb over time or capture other adsorbed species to grow in size. After reaching a critical size, the cluster becomes thermodynamically stable. The number and size of the nuclei grow until a saturation nucleation density is reached, which depends on the energy and number of striking species, the activation energies of adsorption, desorption, thermal diffusion, and the temperature, topography, and chemical nature of the substrate. Usually at this stage the lateral rate of nucleus growth is much higher than the perpendicular

growth rate. The grown nuclei are called islands. Small islands agglomerate to reduce the substrate surface area at a rate that one can accelerate by increasing the surface mobility of the adsorbed species, for instance, by raising the substrate temperature. Larger islands finally coalesce, leaving channels and holes where the substrate is bare. The film structure changes from discontinuous-island to porous-network type while the channels and holes are filled to yield a completely continuous film.

In summary, the successive steps of film growth, namely nucleation, surface-diffusion, two- or three-dimensional nucleation, formation of a network structure, and subsequent filling of holes, result in a continuous thin film. Various growth stages are observed and different growth models apply depending on substrate surface, coverage, film material, and deposition process and conditions. In a simplified categorization, the initial stages (Figure 2) distinguish between the 3-D morphology of island growth (Volmer and Weber [12]), the 2-D morphology of layer-by-layer or step-flow growth (Frank and Van der Merwe [13]), and the two-step layer-plus-island growth whereby a 3-D morphology develops once a 2-D film has reached a critical thickness (Stranski and Krastanov [14]). In almost all practical cases, the island type is the most common process but in polycrystalline thin films and under special conditions other types are observed too.

With increasing thickness, the film acquires its final structure as mainly determined by diffusion at the surface and in the bulk of the film, recrystallization and

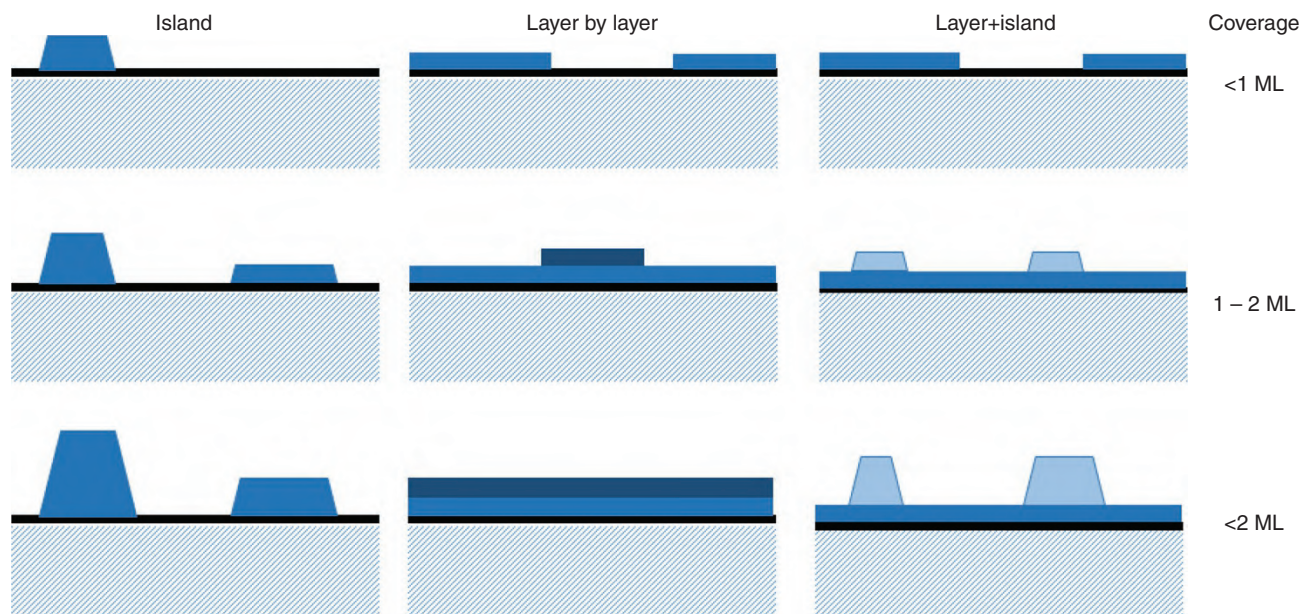


Figure 2 Cross-sections of models of the initial modes of thin-film growth for different surface coverages: island formation (Volmer–Weber), layer-by-layer (Frank–van der Merwe), and layer-plus-island (Stranski–Krastanov) growth.

shadowing effects, which all depend on the substrate temperatures T_s [15]. The growing film develops a local and longer-range structure relative to the substrate, which can be amorphous or polycrystalline and often shows preferred orientation and columnar growth, termed growth texture. Textures influence the film properties through the orientation-dependence of the refractive index or mechanical stress. Concepts to explain differences in such an oriented growth through the so-called structure zone models have been introduced in terms of the ratio between the melting temperature T_m of the film material and the substrate temperature [10]. Structure zone models have also been deduced for sputtered films and for ion-assisted deposition (IAD) [10, 15]. Additionally, the influence of substrate morphology has also been taken into consideration [10, 15, 16].

CVD (and derivative methods such as spray pyrolysis) is the technique used today to deposit coatings *online*, i.e. directly on float-glass lines whose production amounts to several hundred tons per day. Of particular importance thus is the capacity to deposit at high temperatures a wide range of elements at high rates with an excellent adhesion to the substrate. As a matter of fact, online coating deposition is a proven way to manufacture low-cost and durable products from float glass for automotive and architecture.

Another well-established method for manufacturing a wide range of thin films on flat glass is *offline magnetron sputtering*. In the past, glass was sputter-coated after being cut and tempered, usually in its final shape; today, process and material development have allowed this production chain sequence to be changed. In sputtering, the coating species is formed as the recoil product of the collision of a heavy ion with a target of the coating material. The principal advantages of sputtering are the ability to deposit under controlled vacuum conditions either pure metals or metal compounds (nitrides, oxides, etc.) along with the ready availability of highly pure metal targets and various reactant gases. In addition, the possibility of flexible multilayer design allows the optical performance to be optimized as exemplified by thin multilayer systems that can control UV and IR radiation.

3 Thin Films

3.1 Thin Film Materials on Glass and Film Properties

Thin film structures can be engineered today at the atomic level as a result of multidisciplinary research and developments in the fields of vacuum science, solid-state physics and chemistry, surface science, crystal growth, statistical/computational physics, and

characterization methods. The new properties have become the basis of advanced technologies, devices, and industries. The peculiar properties of thin-films of course determine the achievable performance of manufactured products. Although the layers usually consist of well-characterized materials, their properties differ from those in the bulk for three main reasons: (i) these layers are not grown under thermodynamic equilibrium, for example, when the substrate temperature is low or when bombardment energies are high as is the case of IAD techniques; (ii) the high surface-to-volume ratio dramatically changes the physical properties and chemical characteristics; (iii) the optical properties are in addition influenced by the substrate surface and interface morphology. All these quantities are strongly affected by the film preparation method, the chosen parameters, and post-deposition treatments.

Deposition processes depend on a number of parameters that can be varied over broad ranges to ensure predefined physical properties. For PVD processes, these are the deposition rate, the temperature of the glass substrate during deposition or post-deposition annealing, the total gas pressure and partial pressures of the remaining gases and dopant gases in reactive processing, the energy of the deposited particles and bombarding gases, etc.

Thin-film materials for glass coatings are in general grouped into two main categories, namely dielectrics and metals, alloys, semiconductors, and carbon. Dielectrics present an excellent match with the optical performance of glass so that they are preferentially applied as optical coatings. Standard industrial thin-film materials are thus oxides, oxynitrides (e.g. SiO_xN_y), nitrides (Si_3N_4), and carbides (SiC). Oxides such as SiO_2 , Al_2O_3 , HfO_2 , Y_2O_3 , ZrO_2 , Ta_2O_5 , Nb_2O_5 , TiO_2 , ITO (indium-tin oxide), or ZnO are favored because they offer a broad variety of refractive indices and wide spectral ranges of high transmission. Additional advantages are their hardness, abrasion-resistance, and chemical and environmental stability. One may in addition tailor the refractive indices of these films by appropriate oxide mixing. As for SiO_2 films, they have excellent barrier properties, blocking not only the in-diffusion of gases and water but also alkali leaching from the glass [10, 16].

Oxide films are also widely used in multilayer systems. Owing to large differences in refractive indices, the combination of highly refractive TiO_2 with low-index SiO_2 films is commonly used as an efficient broadband reflector in TiO_2 – SiO_2 quarterwave-stack multilayer systems. For multilayer systems with higher accuracy, thermal stability, and lower optical losses, TiO_2 is sometimes replaced by tantalum oxide. Like hafnium oxide, Ta_2O_5 is also a good high-index material for multilayer systems used in the UV spectral region. These materials are often applied for special films in optical applications such as

cold-light mirrors, heat-reflecting filters, color separators, narrow-band interference filters (e.g. dense wavelength division multiplex filters), and laser-optics coatings. To tailor refractive indices, mixtures of oxides are deposited too.

Fluorides (AlF_3 , BaF_2 , CaF_2 , Na_3AlF_6 , DyF_3 , GdF_3 , LaF_3 , MgF_2 , NdF_3 , TbF_3 , and YbF_3) are another class of dielectric thin-film materials used for special UV coatings. Applications at wavelengths below 200 nm are possible because several fluorides have bandgap energies around 10 eV. The materials of choice are magnesium fluoride (MgF_2) and lanthanum fluoride (LaF_3) for low and high refractive-index layers, respectively. Mainly for IR applications, but also for electro-optical devices, sulfide, selenide, and telluride thin films are otherwise of interest (Sb_2S_3 , Sb_2Se_3 , ZnS , ZnSe , ZnTe , CdS , CdSe , CdTe , and PbTe).

Extensive information is needed to characterize adequately thin films, in particular for use in multilayer systems. Since films can have thicknesses in the low nm range and offer little material for analysis, correct basic data for coating materials are difficult to be obtained as analytical methods must be very (surface) sensitive to give reliable results [10]. Macroscopic properties include thickness, refractive index, absorption, light scattering, adhesion to the substrate, stress, density, homogeneity, and hardness; microscopic quantities refer to composition and chemical binding state of elements, stoichiometry, impurities, topography, roughness of surface and interface, formation of interfaces, crystalline or amorphous state, and also the structure of crystals and the local order of noncrystalline materials.

3.2 The Example of TiO_2

Among the great many techniques and materials available to produce the desired optical, mechanical, and chemical film properties, in practice, the choice is determined by specific film requirements. Here, TiO_2 thin films will be used to illustrate such complex interrelations between the properties of the films deposited and the deposition conditions and techniques used. The high refractive index of TiO_2 makes it one of the most important in thin-film materials. It is of interest to commercial products as different as specific interference filters and mass-produced anti-reflecting coatings for shop windows. Now the refractive index of TiO_2 films prepared by different deposition techniques can, for instance, vary by 0.4, a difference that of course influences product performance. These films may in fact contain various foreign elements introduced either intentionally as dopants to adjust properties or, more often, as undesired impurities at various concentrations, in both cases influencing other features such as the crystallization tendency. These impurity

contents are very specific to the deposition process used. In general, they originate from the solutions used in CVD or in the reactive gases and targets in PVD, thus giving valuable information for reverse engineering.

Chemical analyses of the composition do exhibit deviations from the ideal TiO_2 stoichiometry. Compositions of $\text{TiO}_{2.04}\text{Ar}_{0.05}\text{Ta}_{0.003}\text{H}_{0.05}$ and $\text{TiO}_{1.9}\text{Cl}_{0.08}\text{Na}_{0.5}\text{Ca}_{0.01}\text{H}_{0.04}$ have, for instance, been determined for films deposited by sputtering and by sol-gel processes from combined nuclear reaction analyses and Rutherford backscattering spectroscopy [10]. Such data demonstrate that it is meaningless to “know” film properties without careful analyses and an in-depth understanding of the deposition process.

In addition to composition, a core property, another vital parameter is density, which influences many film properties like crystallinity, layer stress, and refractive index (Figure 3). Powerful analytical techniques, such as grazing incidence X-ray reflectometry and Rutherford backscattering spectroscopy are now available to quantify it to high accuracy. Often the density is reported relative to that of a crystalline phase, $\rho_r = \rho_{\text{film}}/\rho_{\text{cryst}}$. With anatase ($\rho_{\text{cryst}} = 3.84 \text{ g/cm}^3$) as a reference for TiO_2 films, one finds that ρ_r , for example, increases from 0.7 for films deposited by dip coating in sol-gel processes (Chapter 8.2) to 1.0 for others made with some advanced PVD and CVD techniques (Figure 4). The densities for other deposition techniques lay between these two extremes although values higher than 1 have even been reported [17, 18].

Most TiO_2 films are amorphous under X-rays but the TiO_2 polymorphs anatase, rutile, and brookite have been observed on float-glass substrates. An increased Na concentration in TiO_2 films, by diffusion from the glass substrate, is essential for the precipitation of anatase and brookite [10, 15]. The onset temperature for crystallization correlates with composition and density. In films of higher density, the formation of dense rutile is favored, which can induce defects [17, 18]. As may be expected, density is to a first approximation directly proportional to the refractive index n and decreasing H (H_2O , OH) content in the film, and also correlates with a change from tensile to compressive stress (allegedly $>1000 \text{ MPa}$ for some PVD films), see Figure 4.

4 Transparent Conducting Oxides

4.1 General Remarks

The two main applications of transparent conducting oxides (TCOs) are the thin films used (i) as electrodes in optically and electrically active systems such as liquid-crystal and organic light-emitting diodes (OLED) flat

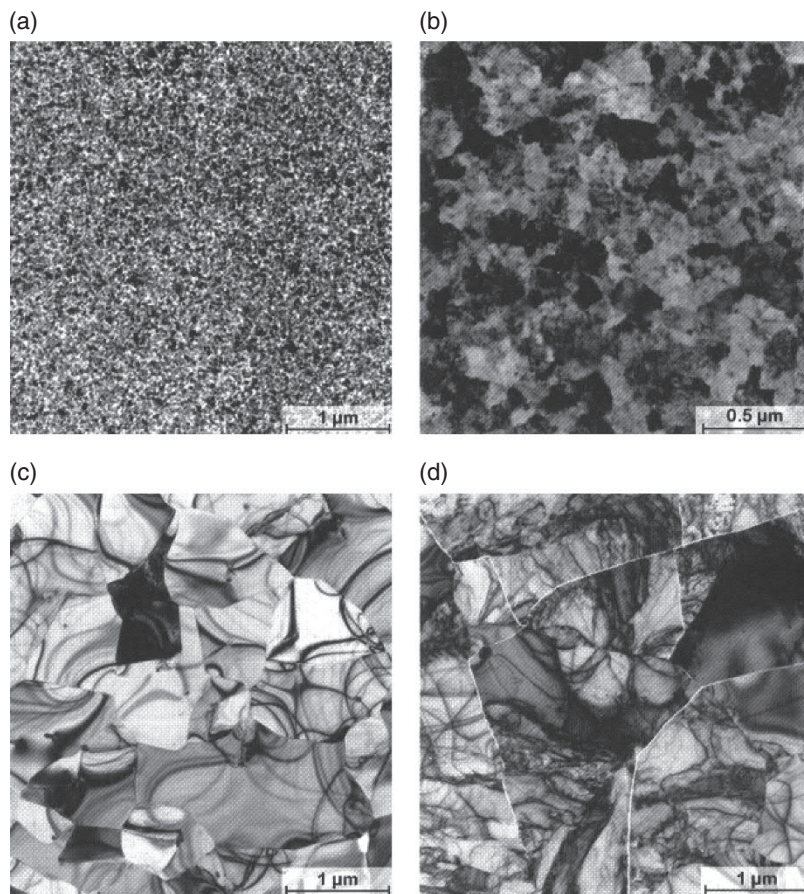


Figure 3 Anatase (TiO_2) thin films deposited at 200°C on float-glass surface as examined by transmission electron microscopy. Small crystal sizes and low densities achieved with (a) sol-gel process and (b) reactive evaporation. Larger crystals and higher densities obtained by (c) ion-assisted deposition and (d) chemical vapor deposition followed by 500°C annealing.

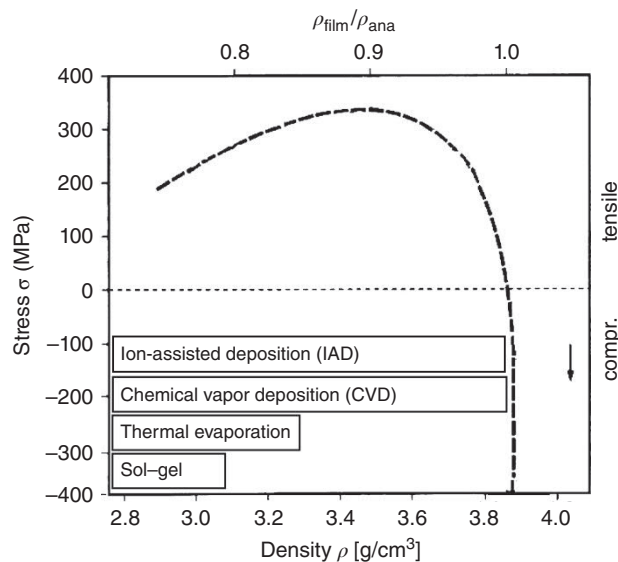


Figure 4 Density ranges of TiO_2 thin films deposited by traditional (sol gel, evaporation) and more advanced (CVD, ion-assisted deposition) techniques and the associated tensile or compressive nature of their internal stresses [17].

panel displays, photovoltaic cells, electrochromic devices, touch screens, etc. (Chapters 6.9 and 6.10) for which ITO is the current industrial standard material; and (ii) for windows in buildings and transportation vehicles to improve thermal insulation, heat preservation, and sun management. Whereas a high electrical conductivity is most important as an enabler for many high-tech products in the first series of applications, the optical properties in the NIR are more relevant in the second.

For very different applications a frequently used thin-film material is SnO_2 . While still hot, newly shaped bottles get, for example, their surface protected by a very thin SnO_2 layer deposited with a CVD process relying on SnCl_4 as a starting material (Chapter 1.5). Likewise, pyrolytic CVD is used online at the float plant to deposit fluorinated tin oxide ($\text{SnO}_2\text{:F}$) at high temperatures to improve the insulating properties of the glass. Besides CVD there are several ways to grow SnO_2 (either doped or un-doped) films on glass, including PLD, DC reactive sputtering, and spray pyrolysis.

4.2 Optoelectronics

Indium oxide doped with Sn (ITO) or Zn, tin oxide doped with F or Sb, and zinc oxide doped with Al, B, or Ga have

the special interest of being electrically conducting substances with a high optical transmission in the visible range. Charge carriers are interstitial metal-ion impurities, oxygen vacancies, and doping ions. Most TCOs are n-type semiconductors where defect/dopant donates electrons to the conduction band, providing charge carriers for the flow of an electric current; p-type TCO materials have also been reported where the defects act as electron acceptors.

For a film of uniform thickness t and resistivity ρ , the sheet resistance R_s can be expressed as $R_s = \rho/t$. For a semiconductor, the resistivity depends on the charge carrier density N and carrier mobility μ as given by the relation $1/\rho = N\mu e$, where e is the electron charge (1.602×10^{-19} C). If N is increased to reduce ρ , the TCO film transmission, especially in the near infrared (NIR), is also reduced because of free-carrier absorption and metal-like reflection so that lowering the TCO resistivity ρ by increasing N adversely lowers the near IR optical transparency of the film. In contrast, increasing the carrier mobility decreases ρ without reducing the NIR transmission.

The effort made to optimize TCO thin-film preparation in recent decades has resulted in leveling off of resistivities at 10^{-4} Ω cm. The most practical materials applied today, the so-called *heavily doped wide bandgap semiconductors* are $\text{In}_2\text{O}_3:\text{Sn}$ (ITO), $\text{SnO}_2:\text{F}$ (FTO), $\text{ZnO}:\text{Al}$ (AZO), and $\text{ZnO}:\text{Ga}$ (GZO). All films have a high transmittance in the visible range, a high infrared reflectance, and a resistivity $\sim 10^{-4}$ Ω cm for thicknesses near 200 nm.

Currently, the industry standard in TCO films is ITO, or tin-doped indium oxide (typically 90% In_2O_3 , 10% SnO_2 by weight), which is used in many electro-optical devices (Chapters 6.9 and 6.10). This heavily doped n-type semiconductor has a large bandgap near 4 eV and is transparent for most visible wavelengths (Figure 5). It is in contrast opaque in the UV (where photons can excite electrons across the bandgap in *band-to-band* absorption) and also in the NIR (where IR photons can excite electrons from near the bottom of the conduction band to higher levels within the same band in *free-carrier* absorption). Ranging from amorphous to crystalline, the structures of the ternary compound ITOs are determined by the deposition conditions prior to the post-process thermal annealing steps applied.

These thin films are deposited mainly by magnetron sputtering (MS) technologies known as direct-current MS (DCMS), pulsed DC MS (PDCMS), high-power pulse MS (HPPMS), and radio-frequency MS (RFMS). Other processes used are ion-assisted plasma evaporation, (low temperature) electron beam evaporation, thermal evaporation, or PLD. Today, deposition on large areas of float-glass sheets is carried out at high rates and moderate processing temperatures; the films exhibit a high optical uniformity and a low resistivity. Since indium is

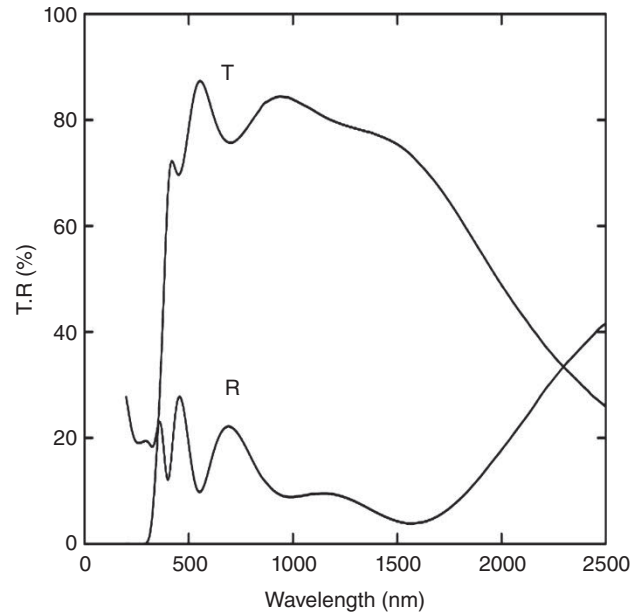


Figure 5 Spectral transmission and reflectance of indium-tin oxide films (thickness: 273 nm; sheet resistance: 16 Ω/sq) on soda-lime glass (Sişecam Science and Technology Center Internal Report 2017).

a rare and expensive metal, the main drawback of ITOs is their cost.

Finally, applications of TCOs to solar-cell technology must also be mentioned. They rely on tin oxide (SnO_2), a wide bandgap semiconductor ($E_g > 3$ eV) that exhibits an optical transparency higher than 85% and has an n-type character conferred by oxygen vacancies. Its electrical conductivity can be significantly enhanced by foreign dopants. The most favored are antimony replacing tin and fluorine substituting for oxygen. The hybrid orbital configurations $2s^2 2p^5$ and $2s^2 2p^4$ for F and O, respectively, suggest that F atoms donate one free electron/molecule when F replaces O. The ionic radius of F^- (1.36 Å) is slightly smaller than that of O^{2-} (1.40 Å), which makes this substitution easy. Actually, F-doped SnO_2 exhibits a good transparency in the visible, owing to its wide bandgap, while retaining a low electrical resistivity due to the high carrier concentration caused by the O vacancies and the substitutional F dopant. Because fluorine-doped transparent oxides are mechanically, chemically, and electrochemically stable, they are used to enhance the efficiency of solar cells as dielectric layers in low-e coatings for windows. Another, unrelated application is in gas sensors which can be divided into two main groups: the first includes sensors that detect oxygen with variations of bulk or surface conductance; the second comprises materials that detect oxidizing and reducing gases in air at constant oxygen partial pressure.

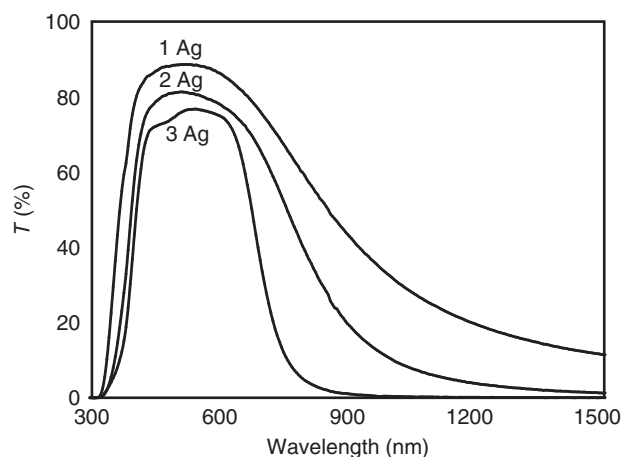


Figure 6 Decrease of light transmission with an increasing number of Ag layers in low-emissivity coatings.

4.3 Low-Emissivity Coatings

Thin films combining a high transparency in the visible with a high reflectance in the far-IR are of special interest for large-area architectural glazing to reduce heat losses from buildings. Their high costs make TCO materials inappropriate for this purpose. Extremely thin metallic coatings (TCM) made with silver or even gold have in contrast become standard in low-e glazing. To achieve the desired properties, these coatings generally consist of dielectric-Ag-dielectric multilayer stacks, where the thin (~10 nm) Ag layer reflects long wavelength IR back into the building (Figure 6). As for the dielectric layers, they act as anti-reflectance devices and they also protect the silver layer, which would not resist corrosion if exposed to air. Low-e coatings are usually deposited off-line by MS, the dielectric layers are commonly made up of TiO_2 , silicon dioxide, zinc oxide, tin oxide, zinc stannate (ZnSnO_3), bismuth oxide or silicon nitride (Figure 7).

Whereas in the semiconducting TCO materials the charge-carrier density controls the NIR transmittance and reflectance of the film, in the TCM approach, the optical response mainly involves absorption by free carriers in the metal. Modern low-e coatings on glass actually comprise 12 or more layers of metals and dielectric materials in a 300 nm-thick stack. In this multilayer system, the films act as interface, base, seed, conducting, barrier, and cover or protection materials. Because the most advanced products incorporate three silver layers and multiple dielectric layers, they are referred to as a *triple silver* low-e coatings. These layer systems markedly reduce the thermal transfer coefficient U . For a 4 mm-thick single pane of float glass, this coefficient is $5.8 \text{ W/m}^2/\text{K}$ whereas a value of $1.0 \text{ W/m}^2/\text{K}$ is obtained for an insulated double-pane coated system. With triple glass

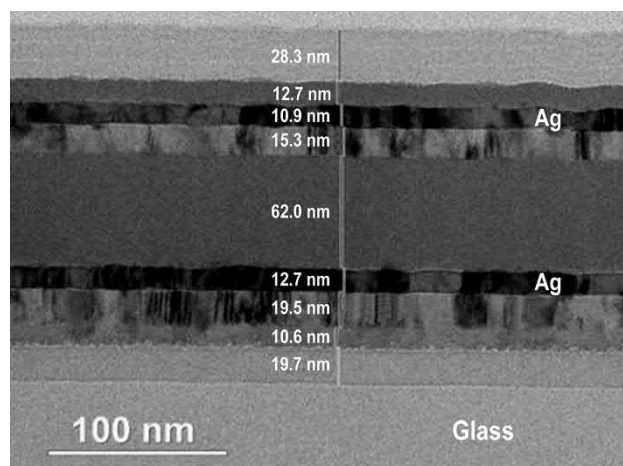


Figure 7 The actual multilayer structure of low-emissivity glasses: the thin Ag layers sandwiched in between oxide dielectric layers seen in a scanning electron microscopy micrograph of the section of a coated float glass.

solutions, the thermal heat-transfer coefficient becomes very close to that of the walls, namely $0.6\text{--}0.7 \text{ W/m}^2/\text{K}$. Heat losses from buildings can thus be reduced by 55 to 70% with double- and triple-pane low-e coated systems, respectively. The energy savings and improvements in carbon footprint made possible by these systems are thus potentially enormous if one thinks that, in the United States alone, about 20–35% of the \$20 billion winter heating bill is wasted by inefficient windows.

The market for low-e coatings has thus grown considerably as a result of environmental legislation and increasing energy costs. In 2016, architectural applications for coated glass amounted to about 18 million tons (~\$24 billion), which were shared between residential buildings (~10 million tons, \$14 billion) and commercial buildings (~8 million tons, \$10 billion). In the years to come, the compound annual growth rate of both segments would be similar at about 6.4%, leading to an annual architectural coated glass demand of almost 24 million tons in 2021. Beside the world major traditional players in coated architectural glass (AGC, Saint-Gobain, NSG, Guardian, Şişecam, Cardinal, and Fuyao), there are also newcomers in the field, especially in Asia (Chapter 9.6). In recent years, competition on the regional scale is crossing borders and becoming global. To expand the market further, the next generation of low-e coatings is increasingly being deposited onto toughenable glass, which is post-deposition annealed at temperatures up to 650°C . Under these conditions, however, Ag atoms are highly mobile so that they can rapidly diffuse through the other layers in the coating stack, compromising their performance.

4.4 Antireflective Glasses

Silicate glasses have a high transmittance in the visible range. But each of their surfaces reflect approximately 4% of the incoming light, which is too high for various applications; the reflectance R of light at an interface between two media of refractive indices n_1 and n_2 is given by $R = [(n_2 - n_1)/(n_2 + n_1)]^2$ (Chapter 6.1) This is the reason why antireflective structures and coatings are needed for most optical components and optoelectronic devices to reduce undesired optical loss and, thus, improve performance. Reducing reflectance has indeed been an important development task for decades. Various approaches are available.

As noted in the Introduction, the potential to reduce reflectivity by modifying the glass surface was realized early. In 1886, John William Strutt, better known as Lord Rayleigh (1842–1912) discovered that aged glasses with tarnished surfaces have a higher light transmittance than new, clean pieces [19]. The reason was that modified surface layers had been created with a refractive index intermediate between those of the glass and vacuum. Today, antireflective glasses can be generated through structuring of the surface (Chapter 6.7) but most applications use coatings, in particular high-quality AR layers, since their very low reflectivity can be tailored for a given wavelength range.

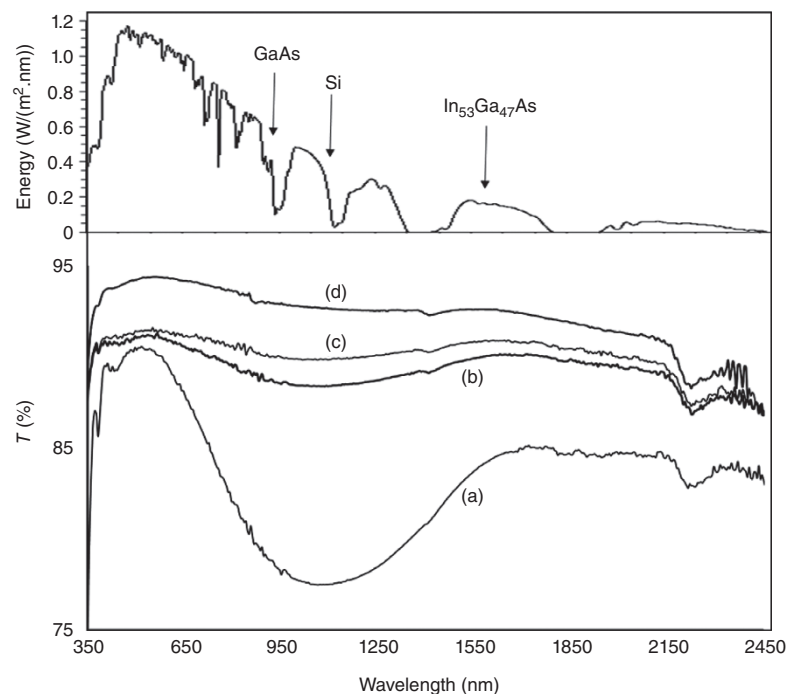
Practical antireflective coatings rely on interference effects in thin layers (Figure 8). Layers with a thickness of one quarter of the wavelength of light ($\lambda/4 = \lambda_0/(4n_1)$), where λ_0 is the vacuum wavelength, lead to a

minimum reflectance for a normally incident beam. These layers are thus called quarter-wave coatings. A destructive interference is also obtained for thicker coating layers ($3\lambda/4$, $5\lambda/4$, etc.). The simplest interference coating thus consists of a *single quarter-wave layer* whose refractive index is the square root of that of the glass. Two reflections of equal magnitude then arise at the two interfaces, and they cancel each other out by destructive interference. Theoretically, the reflectance is zero at the midpoint wavelength (λ) at normal incidence and reduced for a broad range of wavelengths and angles of incidence on either side of the minimum [10]. The most common optical glasses have an index of refraction near 1.52, so that an optimum single layer coating should have an index of 1.23. But no solid thin-film material exists with such a low value. Magnesium fluoride (MgF_2) coatings were often used in the past because they have a relatively low index of 1.38, which reduces the reflectance to 1%. But the material performs much better on a high-index optical glass with $n = 1.9$. This approach has two limitations, however, because (i) coating materials with suitable refractive index are not always available, particularly when the glass has a relatively low refractive index; (ii) and single-layer coating works only over a limited bandwidth (or wavelength range).

4.5 Multilayer Interference Coatings

As already noted, other important devices are made up of alternating layers of a low-index material, like silica

Figure 8 Light transmission of a series of soda-lime float glass: (a) standard 3 mm-thick sheet; (b) low-iron glass; (c) patterned surface; (d) with one-side antireflective film (for photovoltaic applications). Solar spectrum (top) shown for comparison, the bandgaps of some relevant photovoltaic materials being indicated.



(SiO₂), and a higher-index material, like titania (TiO₂). Reflectivities as low as 0.1% can be obtained at a single wavelength. Coatings that give a very low reflectivity over a broad band can also be produced, although these are complex and relatively expensive. Optical coatings can also be made to comply with special characteristics, such as near-zero reflectance at multiple wavelengths or optimum performance at angles of incidence other than 0°. If antireflective properties are required for a very broad wavelength range (or for different wavelength ranges simultaneously, or for different angles of incidence), more complicated designs have to be used, which are usually developed with the help of numerical simulations. As it happens, there is a general trade-off in such multilayer designs between a low residual reflectivity and a large bandwidth. The so-called *V coatings* have a high performance but only for a narrow bandwidth (10 nm), whereas broadband coatings offer moderate performance over a wide wavelength range [10].

5 Miscellaneous Uses

Different types of interference and AR thin-film systems dominate in the information technology area, which are needed for optical communication and integrated optics components such as narrow band filters, wavelength division multiplexers, wave-guiding films, integrated filters, or reflectors in semiconductor lasers. For contrast enhancement and transparent electrodes, antireflective coatings are needed for display glasses. Many other optical devices require such coatings, for example, camera lenses, eyeglasses including those worn for safety and aesthetic reasons, anti-scratch coatings for ophthalmic glasses, sun-protection and photochromic glasses. Flexible substrates with appropriate films are used for touchscreens, iridescent packaging, lightweight mirrors, bendable displays, and light sources (Chapters 6.9 and 6.10). Thin films are applied for energy saving in regenerative lamps or as cold-light reflectors, colored coatings for traffic/railway signal lights, and for both encapsulating and making transparent electrodes for OLED lighting (Chapter 6.10). Optical components for lasers and other instruments use AR interference coatings, beam dividers, mirrors, filters, variable filters, narrow band spectroscopy filters, fluorescence microscopy filters, etc.

In the energy sector, various film systems are applied on float glass for building insulation, in particular conductive low-e films for architectural windows, solar-energy control films for architectural glazing, coating systems for “smart” windows with variable optical properties, and AR coatings for shop windows. A similar broad spectrum of thin-film systems is used for glass applications in

transport (Chapter 9.2). Coatings are used to heat windows and for heat rejection. Reflective coatings for rear-view mirrors in cars have a long tradition but electrochromic mirrors are increasingly replacing them.

In the household, few products use thin films – for cost reasons. But heat-reflecting coatings are applied to oven windows and as oven wall reflectors. In packaging, the glass surface also dominates. Some containers need simple solutions, for instance, coatings to reduce friction, improve scratch resistance, and increase strength. For pharmaceutical packaging, additional functions are needed including transparent diffusion barriers, UV-absorption, and anti-sticking properties for proteins (Chapter 7.7).

6 Perspectives

Glass has long been used in energy technology. For example, the electrical light bulb could not have been invented without it (Chapter 6.9) whereas early electrical distribution networks used glass as an insulator. Hence, it should not come as a surprise that functional coatings on glass are and will be the enabler for many technological solutions to be found to society’s problems regarding generation, conversion, and saving of energy.

In buildings, cost-effective energy saving can be made with glasses that also satisfy environmental requirements, in particular to replace traditional windows which are a “weak link” in the energy consumption of buildings. For decades, the energy balance has been so much improved in industrial countries with low-e coatings on glass that uncoated glass will not find a market for architecture in the future. To contribute to a reduced carbon footprint, the energy-saving properties of passive coatings should nonetheless be improved with more sophisticated multilayer designs relying on materials such as heavily doped wide bandgap semiconductors, metal films and, in the longer term, carbon nanotubes and meshes. Different solutions will employ optically active coatings with more complex materials and processes. The optical properties (transmittance, reflectance, and absorbance) of chromogenic multilayer systems (i.e. electro-, thermo-, photo-, or gasochromic) will, for instance, be adjusted as a function of the charge, temperature, photon, or gas conditions, respectively. Glass may thus be made *switchable* in different ways at different speeds depending on the technology used. Whereas the response takes minutes in the electro-gel sandwiched in the windows of the Boeing 787 Dreamliner, it is extremely short with polymer-dispersed liquid-crystal molecules (Chapter 6.10) in what are still niche applications. To aim at a wider market new technologies are thus under development, for example, plasmon-

enhanced monochromatic or full-color electrochromic switching through arrays of metallic nanoslits [20].

Functional coatings on glass are already key components of state-of-the-art energy conversion systems such as photovoltaics, concentrated solar power, and solar fuel (Chapters 9–0.4). Whereas high environmental stability and transparency are especially needed for concentrated solar power, thin-film photovoltaics made up of Cu(In,Ga)Se₂ or CdTe/Si on thermally stable glass substrates will be a solution in the future. Various other functions will be relevant in this sector. For increasing light efficiency and transmission, anti-reflecting, patterned, or self-cleaning surfaces are, for instance, needed.

In view of the traditionally high energy consumption of lighting devices, the much more efficient OLED technology based on multilayer coatings on glass is rapidly developing (Chapter 6.9). In addition to highly transparent glass, transmitting conductive coatings with high work functions are needed as an anode. For efficient light extraction, glasses with refractive indices higher than 1.8 are to be preferred. To encapsulate the optically active system, a thin film with an excellent barrier function is the solution of choice, particularly for flexible lightweight lighting systems.

Although they are often not visible in the final product, coated glasses are also the enabling component of many products in information technology. Glasses with suitable coatings, as, for example, transparent electrodes, provide the main interface with the users of display or electrochromic devices. More important, coated flexible glass will be the enabler for many future applications, such as high-performance flexible electronics, displays, touch sensors, photovoltaics, or OLED lighting. For various information-technology products, specific film properties are needed, for example, for mobile information systems, scratch-resistant films (reduction of lateral crack generation), and low-friction films to reduce surface fracture initiation.

For transparent conductive films on glass, which are standard in many information-technology devices today, new or improved materials are needed. To obtain an optimized device performance, very specific thin-film properties are required which are strongly correlated with the specific application. For example, for electrochromic systems, the transparent films must be highly conductive (because a high sheet resistance creates a potential drop that causes inhomogeneous coloration), highly transparent (also in the near IR), chemically inert, and provide rapid injection-ejection and collection of charge. For a photovoltaic top electrode, they should be highly transparent in the absorption region of the absorber, have relatively good conductivity (to avoid ohmic drops), and be chemically durable. For liquid-crystal displays (Chapter 6.10), they need only a moderate conductivity,

but a high transparency in the visible range (no haze) and must be particularly chemically stable. For OLED lighting with a highly transparency glass, they must have a high work function because they act as the anode of the device. This flexibility in film properties is only becoming possible with advances in thin-film deposition technologies.

Acknowledgments

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6.9

Glass for Lighting

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1 Introduction

Fire brought light to mankind when it was first mastered about 400 000 years ago and then sustained by any combustible locally available, including animal bones and droppings (e.g. the famous Mongolian *argol*). Only in Antiquity was the torch specially invented for lighting, for instance, in the Roman form of a wooden club on which a mix of sulfur and lime was deposited. Further progress was achieved with *lamps* (from the Greek *lampein*, to shine, which also yielded the Latin *lanterna*) and *candles* (from the Latin *candere*, to shine, and then *candela*, candle) whereby a slowly burning wick generally fed by tallow made much safer and longer lighting possible. Unknowingly to the users, however, what made these flames valuable for lighting were not their maximum temperatures of only 1300–1400 °C, but the soot particles forming as an intermediate step of the combustion process, which emit a rather strong yellow light at these temperatures.

It remained to protect the wick from extinguishment by wind and to prevent the fire from spreading accidentally, which was eventually accomplished in Antiquity with lamps and lanterns. In view of its transparency and non-combustible nature, glass was ideally suited for these appliances. As found in Pompei, transparent glass lamps similar in shape to traditional clay or bronze oil lamps were already made at the beginning of our era [1]. By the fourth century, glass lamps with a metal frame had become common in Italy and the Eastern Mediterranean (Chapter 10.5, [2]). This was especially the case in churches where the natural light coming from large glass

windows was cleverly combined with those of “hundreds of glass lamps set into crown-like structures of precious metal” to guide “the attention of the beholder towards the high altar” [3]. Glass had thus begun a very long career in lighting applications. With new fuels such as whale oil or coal gas, fire lanterns remained well throughout the nineteenth century the only lighting devices in spite of the completely new sources of light that had already been discovered.

Glass had actually played a prominent role in the first of these sources. As observed by Francis Hauksbee (1660–1713) in England and Pierre Polinière (1671–1734) in France, mercury shaken in a Torricelli tube or placed in an evacuated glass vessel connected to a glass electrostatic machine emits a fair amount of visible light (Chapter 10.10), but no attempts were of course made to transpose these *electroluminescence* experiments into practical lighting. Of more immediate interest was thus the discovery of the continuous electric arc made by Vasilii Vladimirovich Petrov (1761–1834) in Saint Petersburg and then by Humphry Davy (1778–1829) in London [4] although the size and cost of the batteries required prevented any extensive applications. It was the invention of the dynamo in 1869 and the availability of relatively inexpensive electric current that eventually opened the way to artificial lighting. Whereas glass was valuable for fire lanterns, it became indispensable for electric lighting because it was the only material available to protect tightly the light source against atmospheric agents without chemically reacting with it, to withstand the heat produced, to absorb as little light as possible, and to obtain readily the shape appropriate for the intended use of the lamp.

Electric arc lamps were ideally suited for public lighting, thanks to their extremely high luminosity, which was originating in the 3600 °C temperature of the arc and strong luminescence of the ionized carbon vapor produced [5]. The first permanent display was made during

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the 1878 *Exposition Universelle* when the electric arc *candles* of the Russian electrochemist Pavel Yablochkov (1847–1894) were installed along the Avenue de l'Opéra in Paris with their glass protecting covers (Figure 1). Although ingenious devices were designed to move continuously and replace the rapidly consumed carbon electrodes, electric arc lamps suffered from UV emission and fire hazards, so their uses became restricted to applications such as search lights (until World War II) for which their extremely high luminosity could not be matched by other means. For other applications, they could not compete with the incandescent lamps and their carbon filaments shining in a glass bulb that were pioneered from the 1830 before being mass produced half a century later, thanks to Thomas Edison (1847–1931) and other inventors, with bulbs first evacuated and from 1913 filled with an inert gas to improve both filament lifetime and luminous efficacy.

As testifies the name *candle* given by Yablochkov to his invention, however, both electric arc and incandescent lighting were still working on the same principle as the

antique oil lamp in that the fuel had simply been replaced by electricity and the wick by carbon electrodes and filaments, respectively. A radical change in lighting applications thus took place when the work done during the last decades of the nineteenth century on electrical discharges in evacuated glass tubes (Chapter 10.10) resulted in the invention of mercury and neon glow lamps more than two centuries after Hauksbee's and Polinière's observations: light was no longer emitted from a small very hot spot but from the whole large volume of a cold device. A better understanding of the atomistic mechanisms of light generation and conversion subsequently led to a number of other innovations. Fluorescent lamps, which convert ultraviolet rays to white light with phosphors (Chapter 7.9), were launched on the market by General Electric in the United States in 1937. Various appliances followed suit, such as tungsten-halogen, sodium, metal-halide, and xenon lamps, and recently solid-state lighting with inorganic and organic diodes. Thanks to better color rendering, improved energy efficiency, and longer lifetimes, they are now widely used for indoor and outdoor lighting, interior lighting for automobiles and other vehicles, and various display devices (Chapter 6.10).

As will be described in this chapter, glass has been involved all these advances because original compositions or forming technologies had to be designed to satisfy the demands of the new light sources (Table 1). A well-known example is the lead borosilicate Nonex (non-expansion) glass invented in 1913 by Corning to solve the very serious problem caused by the breakage of the arc lamps of trains caused by thermal shock under rainy conditions (Chapter 7.6). Whereas transparency (or instead coloration), gas tightness, electrical insulation, mechanical resistance, chemical durability, and versatile formability have kept their fundamental importance, attention has also been paid to thermal resistance and weldability, in particular with metals, which are putting strong constraints both on thermal expansion and on wavelength-conversion properties. In addition, growing environmental concerns have led to the development of new glass compositions free from hazardous elements such as lead and cadmium.

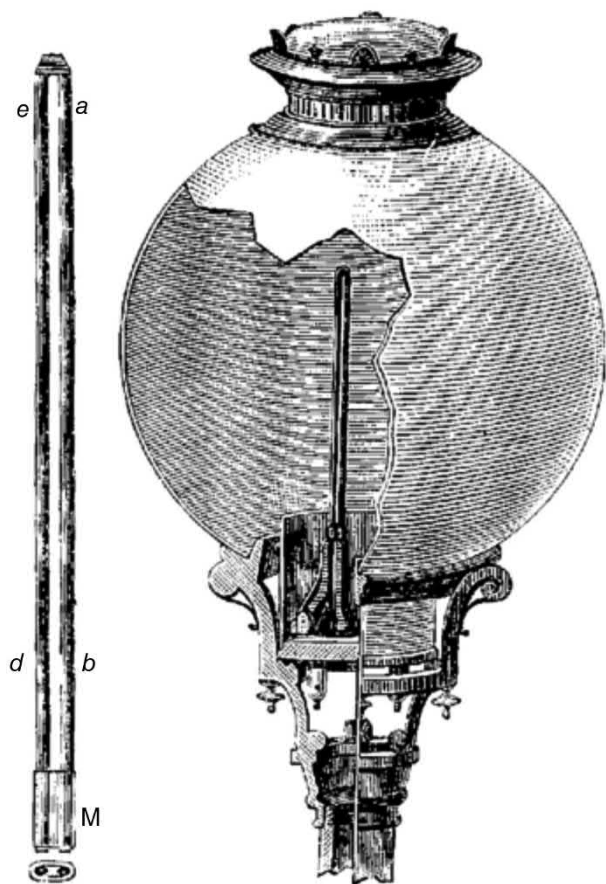


Figure 1 'Yablochkov' candle: an electric arc produced by two carbon electrodes enclosed in a glass bulb [5].

2 Glass for Incandescent and Electric Discharge Lamps

2.1 Incandescent Lamps

Incandescent lighting relies on blackbody emission whose intensity grows as the fourth power of temperature and maximum intensity shifts to shorter wavelengths according to Stefan–Boltzmann law. Operation temperatures must thus be as high as possible to increase both the

Table 1 Chemical composition of glasses for lighting.

		Incandescent lamp								Tungsten-halogen lamp	High-intensity discharge lamp	Xenon lamp	
		Fluorescent lamp											
	Unit	Soda lime	Improved soda lime	Lead	Lead-free	Borosilicate with TiO ₂	Cololed lead and cadmium free	Colored	UV Transmission				
		Alumino-silicate	Boro-silicate	Boro-silicate	Quartz								
SiO ₂	wt %	72	70	58	59	71	68	60	63	57	72	76	100
Al ₂ O ₃		2	2	1	2	3	2	2	2	15	2	1	
B ₂ O ₃			2			16	2	1	2	5	15	16	
MgO		2	3		7		1			6			
CaO		7	6		4		7			8		1	
SrO					6		6			8			
BaO		1			3		3		17				
PbO				29				18			6		
Li ₂ O					2	1	1						
Na ₂ O		16	16	8	8	1	9	11	7		4	4	
K ₂ O		1	2	4	5	8	5	6	8		1	2	
Sb ₂ O ₃			0.2	0.2	0.5			0.2			0.2		
Fe ₂ O ₃								0.1	16 ppm				
P ₂ O ₅			0.3										
MoO ₃							0.2						
S							0.1						
TiO ₂						0.5							
NiO								1.5					
Cr ₂ O ₃								0.7					
Softning temp.	°C	—	693	692	665	710	665	615	686	926	761	771	1660–1680
CTF	×10 ^{−6} /°C		9.9	9.6	9.5	4.9	9.9	10.1	9.6	4.4	3.6	3.8	0.5

intensity of the radiation and the proportion of visible light. Tungsten has long replaced carbon for filaments because it is the pure metal having the highest melting temperature (3400 °C) and lowest vapor pressure along with good mechanical properties at the actual working temperature of about 2500 °C. But the brittle tungsten must be coil-shaped to maximize the surface area of the filament, which is a kind of an engineering feat [6]. Bulbs were initially handblown. Even at rates that could reach 100 pieces per hour and per worker in England in the early 1910s, production was too slow to allow electric lighting to spread rapidly.

Hence, it was mechanization that allowed the United States alone to produce 200 million bulbs in 1919 [7] at a time when glass bulbs represented more than 50% of the sales of Corning [8]. The first machines duplicated the blower's operations: gob gathering by suction, dropping of gob onto blow pipe, blowing and then sagging of parison, and final bulb blowing. In 1923, 11 of the new machines produced over 100 million bulbs in the United States. From 1921 a glass blower named William Woods began to design at Corning a completely different machine, which would remain in use throughout the twentieth century. In 1926 a yield of 300 bulbs per minute was obtained from a continuous glass ribbon originally moving at 0.6 m/s on a series of metal plates, "with one operator, four mechanics, one relief operator, and one transfer mechanic" [8]: holes in the plates allow the glass to sag and be blown (with blow heads and molds moving onto two caterpillar belts at the same rate on both sides of the ribbon) to be eventually cracked off from the rest of ribbon at the cold end of the production line [7].

For the bulb protecting the filament, the glass must have a high electrical resistivity, have a good chemical durability, and be readily sealed with metals and other glasses to ensure excellent tightness with respect to the atmosphere and no or a minimal release of the filling gases. The glass must be highly transparent in the visible range and also, in some cases, in the infrared or ultraviolet, without becoming colored by solarization and UV irradiation. Because resistance to thermal shock is made easier by the thinness of the bulb, a standard soda-lime glass is used, which may be colored if needed (Chapter 6.2). If not, its inner surface is generally coated with colloidal silica microparticles by electrostatic coating to disperse the light evenly. The bulb size increases with the amount of heat to be dissipated, whereas its shape and color depend on whether the lamp is used for interior, automotive, or special lighting, decorative illumination, or electronic equipment. The bulb is tightly sealed with the metal base to be first evacuated and then filled with inert gases to prevent tungsten from oxidizing and evaporating. Along with some nitrogen as an anti-arcing agent, the filling gas is generally argon, occasionally krypton, or even xenon (for lowering tungsten

evaporation by larger atomic size and mass), at a pressure of 80% of the atmospheric value to avoid overpressurization upon use.

Glass is also used for the inner stem that supports the filament, insulates the electric lead-in electric wires and the associated fuse that prevents arcing upon filament breakage, and encloses the exhaust tube serving to evacuate the bulb before filling it with gas (Figure 2). For the stem, lead glasses have been the traditional choice because of their high electrical resistance and formability. For environmental reasons, however, they are now replaced with newly developed lead-free barium- and strontium-bearing compositions. In this case, the mixed-alkali effect on electrical resistance (Chapter 4.2) has served to keep the insulation without affecting the sealing workability and good chemical resistance of the material [9]. Initially lead-in wires also raised a problem because the thermal expansion coefficient of copper of $18 \times 10^{-6} \text{ K}^{-1}$ is two to three times higher than that of the glass. The solution was found in 1911 by means of the so-called Dumet (dual-metal) wire seal, namely, a Ni42–Fe58% core thinly sheathed with brass, enclosed in a copper shell, brazed, drawn to the intended diameter, and finally coated with sodium tetraborate for better wetting with the glass. With a typical 18–28 wt % Cu fraction, the thermal expansion coefficient of the

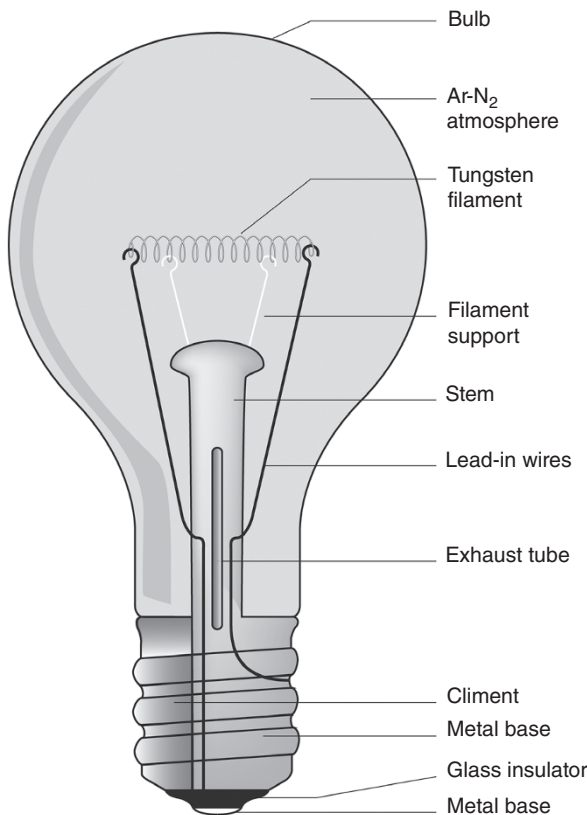


Figure 2 Sketch of an incandescent lamp.

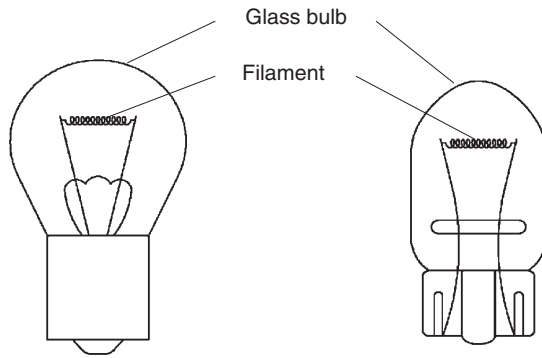


Figure 3 Automotive lamps with either a metal (left) or a wedge (right) base.

wire is about 6.5 and $9.0 \times 10^{-6} \text{ K}^{-1}$ longitudinally and radially, respectively.

For high power or outdoor lamps, the resistance of the bulbs to thermal shock has been achieved with borosilicate glasses whose thermal expansion coefficient is especially low (Chapter 7.6). The sealing metals are then tungsten or molybdenum, whereas the stems are also made up of borosilicate glass. The picture is more complex for automobile (and other transportation) applications because the same lamps are not used for stop lights, direction indicators, room lights, and various types of display illumination. Two types of lamps with different bases are distinguished (Figure 3). With a metal base, the aforementioned soda-lime and lead-free glasses are used for bulbs and stems, respectively. For wedge-base bulbs, a lead-free glass can directly seal the electrodes into glass bulbs, thanks to its good sealing workability and high electric resistance. For direction indicators, a colored glass produces the orange light stipulated by laws and regulations. This orange hue was obtained by addition of CdS-CdSe to the bulb glass. For environmental reasons, however, bulbs for direction indicator lamps are now made with lead-free glass colored with MoS [10].

2.2 Tungsten-Halogen Lamps

The major disadvantage of incandescent lamps is their lighting inefficiency as more than 95% of the energy spent serves to heat the bulb and to emit directly IR radiation, which is why they have been progressively banned in many countries. With tungsten-halogen lamps this efficiency is improved through mixing of bromine or iodine gas with the inert argon or krypton gas filling the bulb (Figure 4). These are the well-known *halogen lamps* featured in households, stores, and especially the headlights of automobiles with their higher luminosity and longer lifetime. They rely on the tungsten-halogen cycle whereby the halogen gas reacts with the tungsten evaporating from

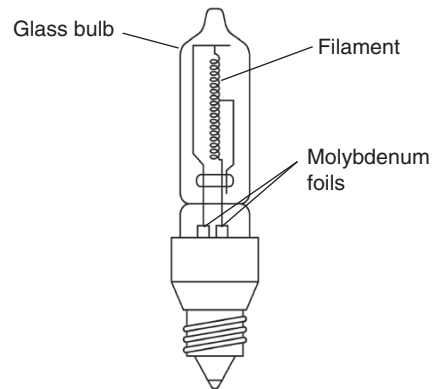


Figure 4 Sketch of a tungsten-halogen lamp.

the filament to form a tungsten halide, which, when brought by convection next to the filament, decomposes on it back into tungsten and halogen gas. Even though tungsten does not deposit only in places where it would be needed, filament damage is limited, and blackening of the glass bulb caused by tungsten deposition is strongly reduced. In turn, these features make it possible to increase the temperature and luminance of the filament and, thus, its efficiency by 30% with respect to its plain incandescent counterparts, for the same lifetime.

To keep the tungsten-halogen cycle going, however, the condition to be respected is that the temperature of the inner wall of the glass bulb remains higher than 250°C , which is the reason for the small size and tubular shape of the bulb. Because temperatures higher than 500°C can obtain in high-power lamps, the tubes are made from high-strain-point glasses able to withstand temperatures of up to $\sim 800^\circ\text{C}$. At such high operating temperatures, water or other gases could diffuse out of the glass and inhibit the halogen cycle. Glasses with water contents lower than 10 ppm are thus required to prevent bulb blackening and to avoid premature failure of the filament. In addition, lamps can be coated with infrared reflective dichroic films such as $\text{TiO}_2\text{-SiO}_2$ or $\text{Ta}_2\text{O}_5\text{-SiO}_2$ to improve the light-emitting efficiency by reflecting back the infrared radiation emitted from filaments whose energy consumption is then reduced.

In general, quartz glass is used for these tubes because of its very high strain and softening points, excellent thermal resistance, and high thermal shock resistance, thanks to its low thermal expansion coefficient. But no metal matches this low expansivity. As a solution, molybdenum foils are used to reduce the stress caused by the expansion mismatch. Quartz glass also transmits ultraviolet rays that would, for instance, result in resin degradation, which is why it is doped with TiO_2 , CeO_2 , etc. or coated with UV-absorbing films. For small halogen lamps, an aluminosilicate glass is used instead along with

molybdenum lead-in wires that match the glass expansivity. In this case, harmful ultraviolet rays are not an issue because they are absorbed by the glass.

2.3 Fluorescent Lamps

Light is emitted in a completely different and more energy-efficient way in discharge fluorescent lamps. Thermal electrons are emitted from tungsten filaments placed at the opposite ends of a tube filled with a low-pressure mercury vapor and an inert gas such as argon, whose ionization increases electrical conduction of the internal space. To enhance the release rate of electrons, the filament is not only coil-shaped but coated with alkaline earth oxide emitters [CaO, BaO, SrO]. When accelerated by an a.c. voltage at high enough energies, the emitted electrons collide along their way with Hg atoms in which they induce a 4.9 eV transition to a higher electronic energy level. Deexcitation then causes the emission of a UV radiation at a wavelength of 253.7 nm. The UV rays are finally transformed into visible light upon impact on phosphors deposited on the inner surface of the glass tube (Figure 5), with which an excellent color rendering may be achieved.

The tubes are shaped with the Danner or Vello processes described in Chapter 7.7. Initially soda-lime glasses were used for straight tubes, and lead glasses for circular, compact, and bulb-shaped tubes requiring good workability during thermal processing for forming bent and complex shapes (Figure 5). As matter of fact, it was

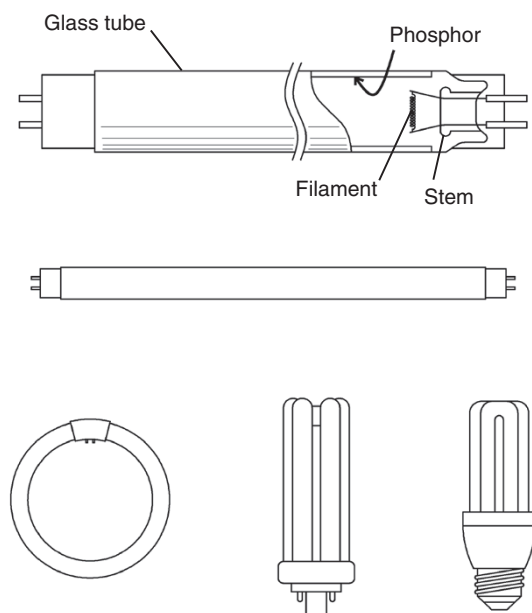


Figure 5 Various types of fluorescent lamps: straight tube, circular line, compact type, and bulb shape.

glass-forming difficulties that prevented compact designs with the same base as for incandescent lamps from being produced earlier than in the late 1990s. Lead glass was also used for the stems of all types requiring good sealing workability and a high electric resistance. A soda-lime-silicate glass containing an appropriate amount of B_2O_3 with excellent workability for forming and sealing has now been developed to reduce these environmental burdens [11] and is used for all types of lamps. A small addition of antimony oxide to the glass composition prevents UV darkening of the bulb.

Cold-cathode fluorescent lamps have been extensively used for the backlight of liquid-crystal displays (Chapter 6.10) until white LEDs were developed. These lamps have a smaller diameter, a greater length, and a higher luminosity, so glass tubes must have a higher thermal resistance and strength during processing. Borosilicate glasses fit well these constraints, but 0.1–5.0 wt % TiO_2 has to be added to the composition [12] to absorb the UV radiation emitted to prevent the transparency of tubes, the light-guiding plate, and reflectors from degrading. As to the lead-in wires, they are made from a Fe–Ni–Co alloy, molybdenum, or tungsten in conjunction with a glass of a matching thermal expansion coefficient.

In the so-called black lights, advantage is in contrast taken of the UV radiation emitted. Along with little or no visible radiations, the long-wave ultraviolet (UVA) produced by these lamps is used in a variety of applications ranging from mineral identification, medical diagnostics, or bacterial disinfection to special lighting effects or the detection of counterfeit banknotes. Glasses colored by nickel and cobalt oxides are used for absorbing the visible light and transmitting only the near ultraviolet at wavelengths of 300–400 nm. For germicidal lamps, a glass with low impurities, especially very low iron oxide content, is alternatively used to transmit UV light at its emission wavelength of 253.7 nm.

2.4 High-Intensity Discharge Lamps

When visible light is produced by the collision of discharged thermal electrons with gaseous metal emitters, another way to increase the efficiency, luminosity, and lifetime consists in increasing the vapor pressure and the temperature within the lamp [13]. Mercury, metal-halide, and high-pressure sodium lamps are such HID devices. They are used for the headlights of automobiles and as light sources for projectors, including interior and exterior wide-area lighting.

These lamps have a complex structure consisting of an outer jacket and a tube within which an electric arc is established between doped tungsten electrodes. After a warm-up period, a light characteristic of the sealed gases

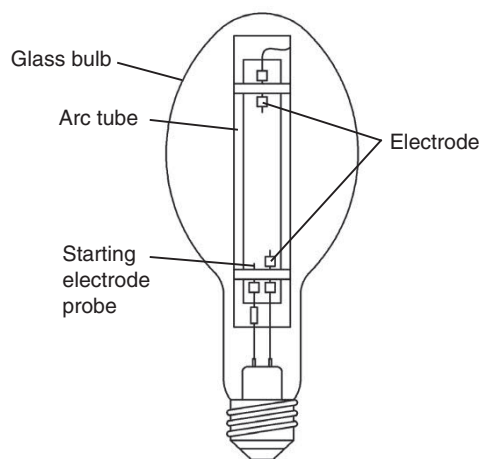


Figure 6 Sketch of a high-pressure mercury lamp.

is emitted (Figure 6). The arc tube is generally made of quartz glass to ensure good thermal resistance and insulation along with a high resistance to devitrification at the high temperatures and pressures of a few tens of bars of operation. It also requires a low content of water, which, if released, would shorten the lamp lifetime and cause failure when discharge is initiated [14]. The jacket maintains the temperature of the arc tube to raise the vapor pressure of the metal and, when filled with nitrogen, to prevent the metal components from being oxidized. Low-expansion borosilicate glass with a high thermal and thermal shock resistance is thus used because temperatures of several hundred degrees can obtain during lighting.

As in fluorescent tubes, argon is also introduced in high-pressure mercury lamps to make discharge easier. Molybdenum foils are used as sealing metals. Upon prolonged operation, strong UV emission would cause contraction and accumulation of tensile stress on the inner surfaces of the outer tubes because of the contraction of glasses containing of B_2O_3 or GeO_2 induced by UV rays [15]. In addition, quartz glass also contracts when exposed to UV rays with a shorter wavelengths and higher energies such as 9 eV [16]. Because mercury lamps generate a light with a bluish white hue, this feature may be eliminated if phosphors emitting red light are deposited on the inner surface of the outer jacket.

In metal-halide lamps the main light emitters are sodium, thallium, and indium bromides and iodides, to which mercury, argon, and various elements are added to enhance electric discharges and improve color rendering. Metal halides evaporate more easily and emit a stronger light than the elemental metal, whereas the lifetime of lamps is prolonged, thanks to the inhibition of the reaction with arc tubes. As an alternative to the usual quartz tubes, alumina ceramic arc tubes have recently

been developed [17] along with Al_2O_3 - Dy_2O_3 - SiO_2 glass-type sealants.

High-pressure sodium lamps are filled with sodium as a luminescent element in addition to mercury and xenon or argon. They emit a specific orange light. A translucent alumina ceramics not reacting with sodium vapor at high temperatures is then selected for the arc tubes. Niobium metals are used as a sealing metal with Al_2O_3 - CaO -type glass frits because they match their thermal expansion coefficient and are highly durable with respect to sodium vapor [18].

2.5 Xenon Lamps

Xenon is another common light source if brought to a pressure of 25–30 bars in electric arc discharges between tungsten electrodes. Quartz glass is again used for the arc tubes, which must be water cooled to dissipate the heat produced by the impact of electrons on the anode. These lamps have an excellent color rendering because their spectral distribution is close to that of natural light. Thanks to their high luminance and long lifetime, they are used for projectors, printing plate making, solar simulators, or analytical instrumentation such as atomic absorption spectrometers (Chapter 5.1). A pulsed light emission is also possible with xenon lamps. Owing to the low amount of heat produced, these can then be miniaturized to serve as flash lamps for cameras. Because the temperature of the light-emitting parts is relatively modest, a low-expansion borosilicate glass can sometimes be used. In this case, tungsten is used as a sealing metal.

3 Glass for Solid-State Lighting

3.1 General Considerations

Solid-state lighting with light-emitting diodes (LEDs) and organic LEDs (OLEDs) is becoming common and even predominant in electronic devices, thanks to an excellent energy efficiency higher than 100 lumens/W combined with a high luminance and a long lifetime. In these latest technologies light is directly emitted by diodes when application of an appropriate current causes excess electrons of an n-type semiconductor (N) to flow and recombine with electron holes of a p-type semiconductor (P). The energy difference between the conduction and valence bands of the N and P regions, respectively, is released not only as heat in Si or Ge but also as light in other semiconductors such as gallium arsenide phosphide [GaAsP] or gallium phosphide [GaP].

After the discovery of this phenomenon of electroluminescence in 1907 on silicon carbide [SiC], much work has been carried out to improve its efficiency and to extend

the range of emission wavelengths, not only directly but also through phosphor fluorescence. A major achievement in this respect has been the invention in 1994 of an InGaN-based semiconductor diode emitting a bright blue light. It became possible to produce radiations of shorter wavelengths for the whole visible part of the spectrum with appropriate phosphors (Chapter 7.9). Further progress has lead lighting with LED to develop steadily since the early 2000s, a growth that is now enhanced by OLEDs. Although solid-state lighting does not need vacuum- or gas-tight containers, it does involve glass. For LEDs, glass is used either as matrix for dispersing and protecting the phosphors that convert the wavelength of the light emitted or as shield for the newly developed quantum dot wavelength converters embedded in resins. For OLEDs, glass is used as both a substrate for the very thin, uniform organic layer and a sealant protecting the organic material from reaction and subsequent degradation with oxygen and water [19].

3.2 Light-Emitting Diodes

In a typical white LED (Figure 7), phosphors convert a part of the blue light emitted, for instance, into yellow with Ce-doped yttrium aluminum garnet (YAG) or into red or green with sulfide or nitride phosphors. The white light then results from combination of these new wavelengths with that of the nonconverted blue light. A mix of these *wavelength-conversion* materials can thus be used to optimize the color rendering properties of the light produced. Another useful implementation is, for example, a combination of a violet LED with red, green, and blue phosphors.

Silicones are common matrices for dispersing these phosphors in LEDs, but they suffer from three main disadvantages. The first is the inhomogeneous distribution of phosphors that results from density difference between

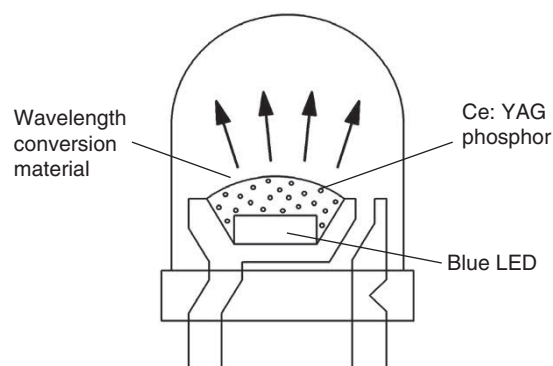


Figure 7 Sketch of a commercial white LED.

the resin and phosphors and prevents the desired chromaticity and luminance from being achieved. The second is the permeability of resins to water, which makes degradation of some types of phosphors possible. And the third is a sensitivity of resins to the heat and strong light generated by LEDs in high-luminance applications, which may result in discoloration and reduced light intensity.

Glass matrices are free from these problems if they are appropriately chosen to avoid reactions with phosphors. New wavelength-conversion materials are thus manufactured from a mixture of glass powder sintered with fluorescent substances. Borosilicate glasses of the type $\text{SiO}_2\text{--B}_2\text{O}_3\text{--RO}$ [$\text{R} = \text{Mg, Ca, Zn, Sr, Ba}$] can, for instance, be used to sinter Ce-doped YAG. At lower temperatures $\text{SiO}_2\text{--B}_2\text{O}_3\text{--ZnO}$ and $\text{SnO--P}_2\text{O}_5\text{--B}_2\text{O}_3$ glasses can be alternatively selected for sulfide or nitride phosphors. A more uniform dispersion phosphors is achieved with these glasses, which makes it possible to control precisely the chromaticity and luminance through adjustment in the material thickness in the desired shape (e.g. plate, bar, dome, etc.). In addition, a higher luminous efficiency results from the dispersion of the excitation light by the phase boundaries, bubbles, and microcrystals generated by the sintering process, whereas the glass gas tightness prevents oxygen and water from penetrating the material and degrading the phosphors. Finally, such glass-based materials are highly resistant against discoloration and deterioration even when used for high-luminance applications [20, 21].

3.3 Quantum Dot Light-Emitting Diodes Backlight

In ongoing advances, attention is being paid to *quantum dots*, namely, tiny semiconductor particles whose nanometer size give them special electronic and optical properties, which are intermediate between those of isolated atoms or molecules and of bulk semiconductors. By adjusting the size of the quantum dots (Chapter 6.8), one can in particular tune their fluorescence wavelength and, thus, obtain more vivid images through a finer reproduction of the range of colors as done in the backlight of a liquid-crystal display panel (Chapter 6.10).

A disadvantage of quantum dot fluorescent substances is low resistance to water, however, which makes these phosphors liable to fast deterioration when dispersed in a resin matrix. A new sealing technology with glass thus is under development to avoid the problem (Figure 8). The package contains a quantum dot–resin matrix, which is itself protected against water by a glass seal. The package must be laser sealed to avoid the heat damage on

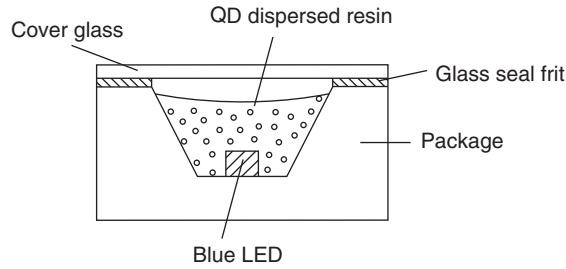


Figure 8 A quantum dot packaging under development.

either the quantum dots or the embedding resin that would result from ordinary sealing processes at several hundred degrees Centigrade. Upon laser sealing, in contrast, the glass is specifically heated by absorption at the wavelength of the laser beam, so its interior remains unheated [22, 23].

3.4 Organic Light-Emitting Diodes

With respect to LEDs, OLEDs feature still lower power consumption and better color rendering with the light emitted by electroluminescent organic substances such as polyfluorenes $[(C_{13}H_8)_n]$ or poly[*p*-phenylene vinylene], PPV $[(C_8H_6)_n]$. In contrast to LEDs, they are not bright point sources but extended surface lights [24]. They are currently incorporated in flat display panels (Chapter 6.10), but previous work has also made use of them as transparent lighting panels, for instance, inserted in windows.

Because of its relatively high electrical resistivity, the electroluminescent substance is inserted in the form of a thin film sandwiched between two thin-film electrodes, at least one of them being transparent (the anode, made up of indium-tin oxide [ITO]). When an electric field is applied between these electrodes, electron holes are injected by the anode into the emissive layer where they recombine as excitons with electrons coming from the cathode, which then release light and heat when relaxing to the ground state of the valence band (Figure 9). In practice, two additional films are inserted between the electrodes and the emissive layer to optimize hole and electron transport, whereas some transition metals are added to the emissive layer to improve light production by excitation relaxation. As to the whole assembly, it must rest on a substrate that must perfectly smooth and have a constant thickness, which can be made of metal, resin, or glass.

The emissive layer is highly sensitive to water and oxygen, which makes in principle glass preferable to resins for transparent, gas-tight substrates. In contrast to glass, however, resins are flexible, which makes the design of

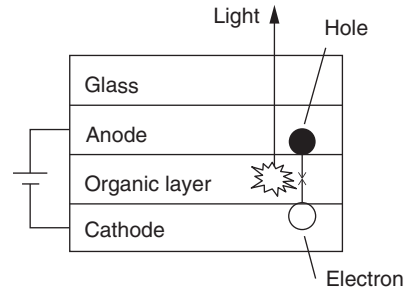


Figure 9 A simplified sketch of the light-emitting mechanism of an OLED.

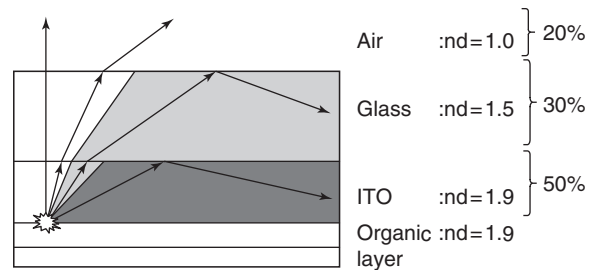


Figure 10 Effects of the indices of refraction of the glass substrate and ITO electrode on the light exiting from and remained trapped in an OLED.

bendable OLEDs possible and in addition allows for continuous production process from rolls instead of plates to improve productivity. For improved bendable OLED lighting, a non-alkaline aluminoborosilicate glass substrate has thus been developed and is produced by the overflow downdraw method (Chapter 1.4) with a 50–100 μm thickness for which a roll-to-roll process is under development [25].

Currently the most important issue is to increase the emitting efficiency of OLEDs by reduction of the mismatch between the refractive indices of their structural components. With an index of about 1.5 for the glass substrate and values ranging from 1.9 to 2.1 for the emissive layer and ITO electrodes, the incident light at angles greater than critical angle cannot transmit the substrate, so the lighting efficiency is limited to about 20% (Figure 10). One can thus make a glass substrate with a higher refractive index by incorporating SrO , BaO , ZrO_2 , TiO_2 , La_2O_3 , or ZnO into the composition. Alternatively, one can achieve a high refractive index by grazing powdered glass so as to increase the critical angle at the substrate–electrode interface [26] and, thus, to increase the amount of light transmitted. As a matter of fact (Figure 10), the latter design can be combined with

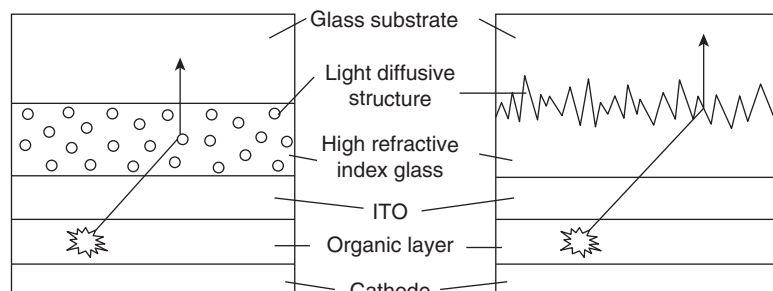


Figure 11 Inclusion of a highly refractive glass and a light-diffusive structure for improving the amount of light actually produced by an OLED.

the addition of a scattering layer to raise further the efficiency of light extraction from the substrate to the air [27–29]. Of course, the aforementioned laser technology can also be used for sealing the substrate without needing a drying agent [30].

4 Perspectives

To summarize the advances made in lighting devices throughout the ages, it will suffice to mention that candles typically have a luminous efficacy of about 0.2 lm/W, incandescent bulbs of 8–15 lm/W, fluorescent tubes of 70–100 lm/W, high-pressure sodium lamps of 90–150 lm/W, and LEDs of 100–170 lm/W, whereas the luminous efficiency (i.e. the fraction of energy not lost as heat) has in parallel increased from 0.05 to 30%. In this history, a striking feature has been that major improvements in century-old lamps have been made shortly before they became obsolete. The 5–10 times more luminous version of the oil lamp with a hollow circular wick, a glass chimney, and air control was, for instance, invented in 1780 by Ami Argand (1750–1803) in Geneva. Likewise, mechanization of candle production was achieved only at the beginning of the nineteenth century when electric lighting was about to be invented. Since then improvements have been much more rapidly as exemplified by the coiled tungsten filament used in incandescent bulb from the late 1910s, which has then be used in fluorescent and other lamps. Particularly in the last three decades, the rate of innovation has considerably accelerated, thanks to the advances made in both basic physics and materials engineering. The miniaturization of light sources down to the pixel size that has been at the roots of the recent display revolution is especially noteworthy (Chapter 6.10).

Along this evolution glass engineers have always found the solutions to the original problems raised either by these new light sources or by their improvements with respect to energy efficiency or color rendering through the obtained wavelength distribution. In these advances, composition has been as usual the main factor acted upon

to achieve the desired properties, but other important progress had also to be made in terms of processes, for example, to produce the stable ultrathin glass sheet used in flexible devices. Since all efficient luminescent phenomena currently known have been put to use in lighting devices, it is not easy to guess what kind of new light sources could be invented. But glass scientists and engineer can nonetheless feel confident that they will be able to solve the new problems that would be raised by new lamps in terms of both properties and processes. Such a new problem is in fact currently raised by quantum dots, which are less heat resistant than conventional phosphors, so new glasses have to be developed with low softening point and sintering temperatures to achieve a high luminous efficiency and a long life expectancy.

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6.10

Screens and Displays

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1 Introduction

From computer screens to cell phones and from TV sets to advertisement panels, the ubiquity of information displays is one of the most visible manifestations of the late twentieth-century electronic revolution. What might be less obvious, however, is that glass is a critical component of all these devices (Figure 1). Ever since the beginnings of artificial lighting, glass has in fact been such a component because it is the only material available to protect the light source against atmospheric agents without chemically reacting with it, to absorb as little light as possible, and to obtain readily the shape appropriate for the intended use (Chapter 6.9). These advantages are of course still put to use in modern displays, but additional and much tighter material constraints have now to be satisfied because of the complex ways in which large, high-resolution images are generated in flat-panel displays (FPD).

Of particular importance are the heat treatments performed at temperatures as high as 600 °C during the fabrication process to deposit on glass surfaces the various elements required for color light emission. Such features have made it necessary to develop new, alkali-free glass compositions with higher strain points such that, through greater thermal stability, irreversible high-temperature deformation is avoided. Likewise, chemical durability has been improved to allow for more aggressive etching of glass surfaces and, thus, to speed up the fabrication process and ensure better adhesion of the deposited

devices. Finally, efforts have also been made to lower density and, thus, to reduce both gravitational sag and the weight of the appliances and also to match better the coefficient of thermal expansion of the glass with that of the silicon of the electronic chips.

Because it has dominated the display industry for more than half a century with billions of TV sets produced, cathode-ray tubes (CRT) will be described first. One of their main limitations is their large volume since they must be deep enough to allow electrons to be accelerated at speeds such that luminescent ions deposited on a glass screen are excited upon impact to produce images. Turning to FPDs, the manner in which material constraints have been satisfied will then be dealt with in the rest of this chapter. To produce them, the first solution was to rely on a backlight to excite much more sensitive substances than phosphors, namely, liquid crystals. Following liquid-crystal displays (LCD) in the early 1990s, further advances have been made with plasma-display panels (PDP) and then organic light-emitting diode (OLED) panels whose higher luminosity and brightness is ensured by light production on the screen itself.

After their appearance in the early 1990s, FPDs have dominated the market as early as in the mid-2000s, thanks to their large size combined with low volume, operating voltage, energy consumption, environmental and breakage hazards, and even fabrication costs. For all of these displays, the race toward larger panels has also required improvements in the production process to reduce considerably the density of glass defects. This topic is beyond the scope of this chapter, however, because the two main processes used for making FPD glass, namely, float and drawdown, are described in Chapter 1.4. It will suffice here to summarize the very rapid advances made in this respect by the increase

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during the last two decades of the biggest LCD panels commercialized (Figure 2), a trend that has been paralleled by a large and continuous decrease of production costs. Likewise, the way in which visible light is emitted by phosphors deposited on screens in CRTs and PDPs will not be dealt with because the luminescence process involved is described in Chapter 6.3. We will simply note that a great many different inorganic luminescent materials may be deposited on the glass screen (e.g. $\text{Y}_2\text{O}_3\text{:Eu}$, $\text{Zn}_2\text{SiO}_4\text{:Mn}$) with a grain size a few microns.

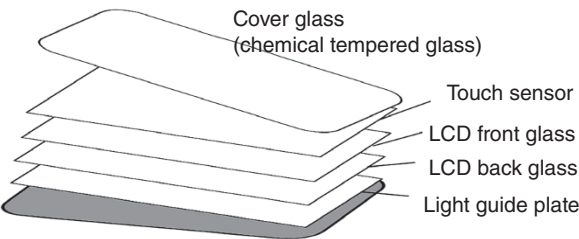


Figure 1 The many different functions of glass in a cellular phone. The example of liquid-crystal display: cover for protection of the device against scratches and shocks, touch sensor for detection of the user's commands, front glass for the color filter creating the image, back glass for supporting all thin-film transistors (one per pixel), and guide plate for transmission of the light produced at the edge of the device to the liquid crystals.

Acronyms

CRT	cathode-ray tube
CTE	coefficient of thermal expansion
FDP	flat-panel display
ITO	indium-tin oxide
LCD	liquid-crystal display
OLED	organic light-emitting diodes
PC	personal computer
PDP	plasma-display panel
TFT	thin-film transistor

2 Cathode-Ray Tubes

Television has been a by-product of the physics revolution of the late nineteenth century when the study of electrical conductivity in rarefied gases enclosed in glass vessels led to the discovery of the so-called radiant matter. When an absorbing obstacle was inserted along its pathway, a striking feature was that one would observe its shadow image at the other end of the tube (Figure 3). Radiant matter then became termed cathode rays, whose impact on the other side of the glass vessel resulted in the emission of X-rays as first observed by Wilhelm Röntgen (1845–1923) in 1895 in Würzburg (Chapter 10.10). Shortly after, cathode rays turned up to be electrons

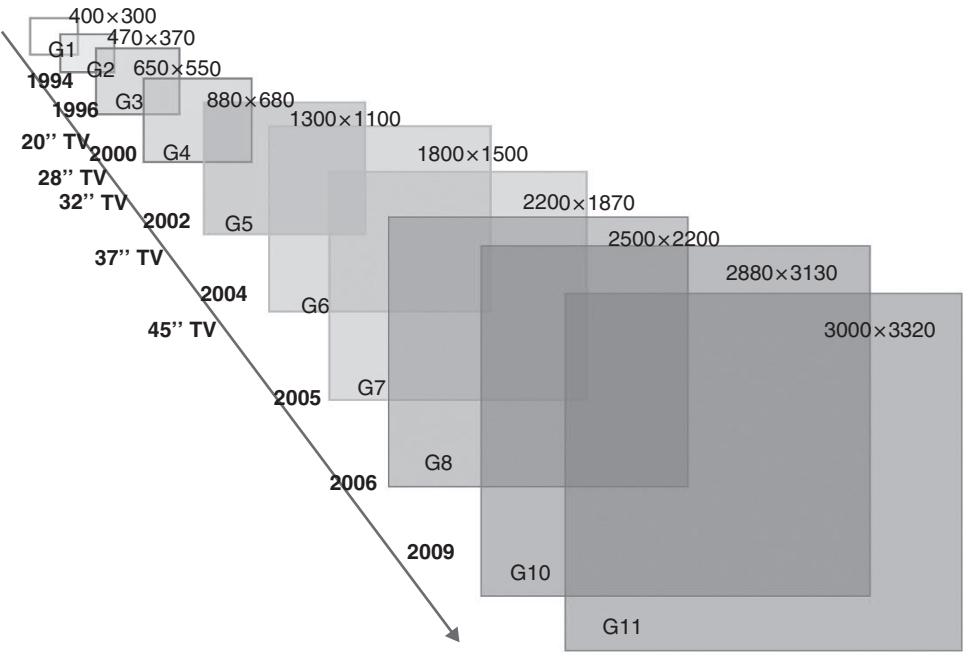
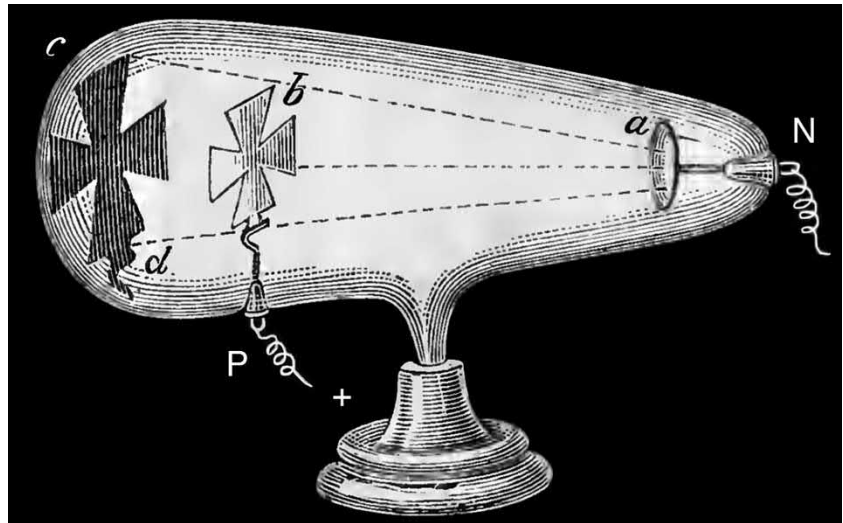


Figure 2 Size increase with time of mother glass in TFT-LCD.

Figure 3 An early image produced by William Crookes (1832–1919) with a cathode-ray tube: electrons emitted by the heated cathode and accelerated toward the cross-shaped anode whose shadow is seen at the other end of the tube [1].



accelerated between the cathode and anode, the first sub-atomic particles discovered by Joseph John Thomson (1856–1940) in 1897 in Cambridge.

Going from the primitive static image of Figure 3 to dynamic ones might seem to have been a real challenge. As soon as 1897, however, the German physicist of radio-wave fame Karl Ferdinand Braun (1850–1918) took advantage of the known deflection of cathode rays by magnetic fields to visualize current and voltage waveforms in two dimensions on a mica plate coated with a phosphorus paint; the trick was to deflect a narrowly collimated beam with the modulated field created by a coil whose axis was perpendicular to that of the glass tube.

The use of the back panel as a screen then made the oscilloscope the very first imaging instrument (actually with electrostatic deflection by two pairs of vertical and horizontal plates). To design a television – a term coined in 1900 in French by the Russian scientist Constantin Perskyi (1854–1906), the following step was to transform an image into an electric current and to form it back on a screen. In 1907, Boris Rosing (1869–1933), for instance, used in St. Petersburg an alkali metal photocell for his *electric telescope*. Through intense international competition, further progress in image scanning and signal amplification allowed the first radio-transmitted images to be broadcasted with a resolution of a few tens of lines by John Logie Baird (1888–1946) in London or Kenjiro Takayanagi (1899–1990) in Japan in 1926. Although the first commercial broadcast of television took place in England in 1937, it was only after World War II that TV sets became household fixtures with an improved resolution of more than 500 lines. Color pictures were then

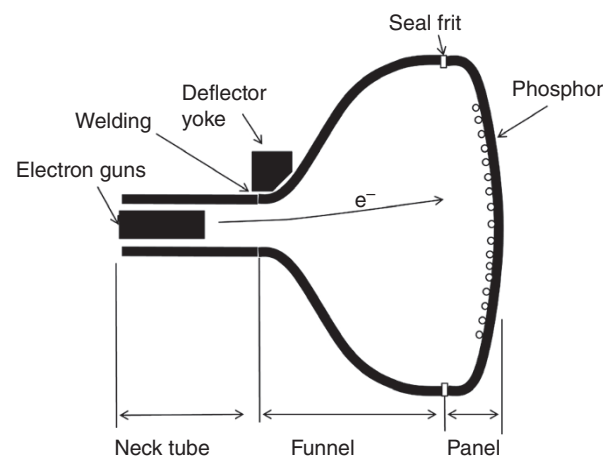


Figure 4 Sketch of a television cathode-ray tube.

produced in the 1960s with three distinct electron guns for red, green, and blue, whereas the resolution later increased up to 1000 lines.

Three different parts constitute a CRT (Figure 4), namely, the neck, shaped by drawing, where the electron guns are located; the panel, shaped by pressing, where the image is formed; and the funnel connecting them, also formed by pressing. Obvious material prerequisites are that the evacuated glass tubes sustain the atmospheric pressure exerted and strongly absorb the X-rays emitted to prevent them from being transmitted to the viewers. In addition, the glass must have a specific light transmittance that does not degrade upon irradiation by electrons and X-rays as well as a high enough volume electrical

Table 1 Chemical composition (wt %) of glasses for color cathode-ray tubes.

	Panel	Funnel	Neck	Seal
SiO ₂	60.5	50	50	3.4
Al ₂ O ₃	2	4	1	
B ₂ O ₃				8.6
Na ₂ O	8	6	2	
K ₂ O	7.5	8.5	10	
MgO		2		
CaO		4	2	
SrO	9.5	1		
BaO	9	1		1.7
PbO		23	34	71.1
ZnO	0.5			13.7
TiO ₂	0.5			
ZrO ₂	1.5			1.4
CeO ₂	0.2			
Sb ₂ O ₃	0.3	0.3	0.3	
Fe ₂ O ₃	0.1			
CTE (ppm/°C)	10	10	10	10
Softening point (°C)				344

resistivity to maintain electrical insulation in spite of the high accelerating voltages applied.

All these constraints are satisfied by glasses bearing high contents of heavy metals (Table 1, [2]). The X-ray absorbance must in fact be higher for color than for monochrome TV because a higher accelerating voltage (30 vs. 20 kV) is required as an important fraction of the electrons emitted is absorbed by shadow masks that remove those that would otherwise impact the wrong phosphors. Lead is by far the most efficient absorbing element (Table 2), but it has been restricted to the neck, the thinnest part, because of yellow color centers produced upon irradiation and of environmental concerns about recycling after use (Chapter 9.8). The less problematic barium and strontium are thus used for the thicker funnel and panel.

The funnel and the neck glasses can be mutually welded because their compositions and softening temperatures of about 650 °C are very close. With a higher softening point of about 700 °C, the panel glass must in contrast be sealed with a low-melting glass frit whose typical composition is included in Table 1 [3]. Finally, special attention must also be paid to the thermal expansion coefficients (CTEs) of both parts to minimize thermal stress and, thus, failure problems.

Table 2 Effect of cation atomic weight on the mass absorption coefficients of the main metal oxides at a wavelength of 0.06 nm [2].

Oxide	Mass absorption coefficient
SiO ₂	2.343
Al ₂ O ₃	2.114
Li ₂ O	0.553
Na ₂ O	1.687
K ₂ O	8.446
MgO	1.920
CaO	8.809
SrO	53.407
BaO	25.081
PbO	82.866
ZnO	28.540
TiO ₂	9.123
ZrO ₂	53.535
CeO ₂	25.318
Sb ₂ O ₃	18.188

3 Glasses for Flat-Panel Displays

3.1 General Considerations

Schematically, the function of glass in a CRT is to be an evacuated vessel in which electrons freely propagate until they hit at one of its ends a screen on which phosphors have been deposited to produce images. Except for forming processes and compositional adjustments required for X-ray absorption, these two functions did not require special technological advances. The situation has been quite different with FPDs for which really new glasses and processes had to be designed.

First, devices such as cell phones and tablet computers require cover glasses to be resistant to wear and consistent with the so-called touch-display technologies. Second, the strong customer demand for thin and lightweight devices requires to use thinner glass panels without compromising their physical properties. Third, the image information is no longer transmitted as modulated electrical currents (deflecting electron beams) but as digital bits that must be transformed back into visible electromagnetic radiations on the screen itself: to command individually each pixel, X–Y arrays of tiny electrodes are needed, which must in addition be transparent. Fourth, upon use the glass must not react in any way with the other components of

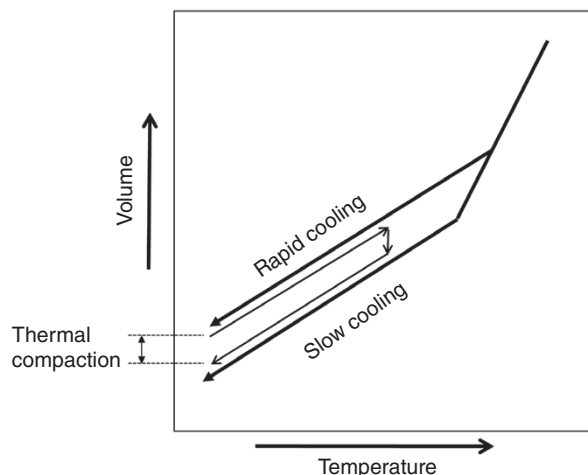


Figure 5 Thermal compaction of a glass upon structural relaxation in the glass transition range.

the screen. And fifth, as already noted, the various devices used to produce light pixels are implanted through high-temperature treatments after which the relative positions of two given points on the panel should be constant to within about $1\ \mu\text{m}$.

3.2 The Problem of Thermal Compaction

In high-temperature treatments of glass, the major problem encountered results from volume relaxation if the glass transition range is approached (Figure 5; see also Chapter 3.5). Known as thermal compaction, this effect is due to the fact that the volume of the glass then tends to relax to its equilibrium value. Because the fictive temperature of the glass is necessarily higher than the treatment temperature, the result is a volume decrease at a rate and by an amount that both depend on the difference between these two temperatures and also on glass composition. The most efficient way to limit the effect is of course to increase the glass transition temperature through compositional modifications.

The problem is especially important in the fabrication of PDPs, whose process requires maximum temperatures of around $600\ ^\circ\text{C}$ that exceeds the strain point of the substrate glass. A comparison of these effects is made for a soda-lime glass and a high-strain-point glass specially designed for PDPs [4] whose strain points are 511 and $570\ ^\circ\text{C}$, respectively (Figure 6). Since the relaxation rate is higher when the glass is heat treated at higher temperatures, thermal compaction becomes more important as the treatment temperature increases. Thermal compaction apparently decreases

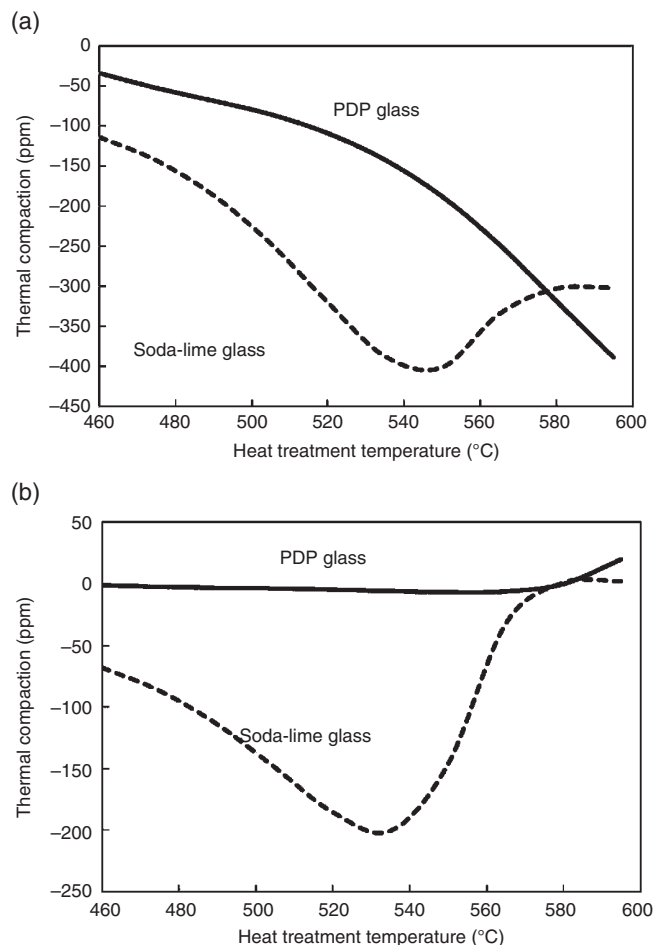


Figure 6 Thermal compaction upon annealing near the glass transition range. Comparisons between the volumes of a soda-lime glass and a PDP substrate upon annealing (a) and upon reheating (b) after the annealing treatment shown in (a).

above $540\ ^\circ\text{C}$ for the soda-lime glass, however, simply because complete relaxation is achieved in this region that is close to the glass transition temperature of $550\ ^\circ\text{C}$. In other words, the soda-lime glass is no longer an elastic material and undergoes instead a permanent thermal deformation that spoils the panel fabricating process. Although the magnitude of thermal compaction increases at 550 – $600\ ^\circ\text{C}$ for the high-strain-point glass, the effect is not problematic for the process because it is homogeneous and reproducible upon well-controlled thermal conditions. In addition, it can be minimized by a two-step process whereby the glass is first heated in the glass transition range (Figure 6b). Such high-strain-point glass has thus enabled mass production of the large-sized PDPs with the required thermal stability.

Table 3 Chemical compositions (wt %) of frit glasses for PDP.

	Underlayer dielectric	Overlayer dielectric	Barrier rib	Pb-free barrier rib	Sealing
SiO ₂	28.4	8.0	37.2	11.2	3.3
Al ₂ O ₃		0.6	0.7		1.0
B ₂ O ₃	1.8	16.2		44.1	8.8
BaO					1.7
PbO	69.8	67.7	62.1		76.9
ZnO		7.5		41.2	10.0
Li ₂ O				3.5	
Softening point (°C)	576	471	580	533	372

3.3 Glass Frits

Glass frits are also important for realizing high-performance display devices. As described above, they were first used as a sealing glass in CRTs. They are still more important for PDPs where they serve to make key such parts as dielectric layers and barrier ribs (Table 3). They are printed on the glass substrate and patterned by sand blast or UV-lithography technologies before being fired at 500–600 °C and sealed with a glass similar to that used for CRTs. Their compositions have been optimized with regard to thermal expansion for thermal stability, absence of lead for environmental concerns, and low firing temperatures for economic reasons.

3.4 Front Cover Glass

Ever since the first smartphones were launched in the market in the early 2000s, a strong demand has manifested itself for tough, lightweight cover glasses. The main concerns were to ensure resistance to shocks (e.g. fall on the ground) and to prevent scratches from accumulating and making display reading difficult. Chemical tempering was the obvious solution because the process is not only the most efficient but also applicable to thin glass sheets as well as to products with a complex shape (Chapter 3.12). The appropriate surface compressive stress and the thickness of the ion-exchanged layer have been designed from fracture analyses [5] although a really fundamental understanding of stress generation and relaxation by ion exchange are still important issues [6]. As might be expected, these chemically tempered glasses are also used for tablet Cs and flat LCD TVs. Currently Corning, AGC, Nippon Electric Glass, and Schott AG are well-known companies that supply them.

3.5 Drivers: Glass for TFT Arrays

Drivers are electronic components controlling all elements of the displaying matrix device. They differ

depending on whether matrix addressing is passive or active although in both cases an $n \times m$ display is addressed by $m + n$ control signals. With a passive matrix, a pixel is maintained in the same state until it is refreshed; the drivers then are simply two series of electrodes lying at right angles on the glass substrate, which can be made of soda-lime glass. Commercial display devices usually rely instead on an active matrix, however, with which the state of each pixel is actively controlled by a thin-film transistor (TFT) and capacitor to avoid *crosstalk*, i.e. inadvertent pixel state changes, and, thus, to ensure a better picture quality.

These transistors are made of amorphous Si, polycrystalline Si, or oxide semiconductors such as In–Ga–Zn oxide as described in the literature [7, 8]. In the process, material deposition and etching are necessary steps because the gate bus lines, TFT channels, data lines, passivation, contact hole openings, and pixel electrodes are directly formed on the glass substrate. Hence the glass must be thermally and chemically stable at the temperatures and under the etching conditions relevant to the panel manufacture process. New glasses have thus been developed to satisfy these requirements through higher strain points and lower densities.

Thermal compaction is one of the factors that must be considered seriously. When the thin-film transistors of Liquid-Crystal Displays are made of amorphous silicon, the process temperatures of only 300–350°C [9] are unproblematic. Thermal compaction is, in contrast, a really critical issue when the thin-film transistors are made of polycrystalline silicon because much higher process temperatures of 550–600°C are then required. Some thin-films that include indium-tin-oxide (ITO) transparent electrodes are deposited and patterned on the glass substrate (Chapter 6.8). Mechanical properties, including easy scribing, are also an important issue for the glass substrates in the LCD and OLED panel manufacturing process [10] because multiple arrays formed on the substrate glass need to be separated correctly from one another.

Table 4 Properties of glass substrates for thin-film transistor liquid-crystal displays.

Company	Code	Density (g/cm ³)	Strain point (°C)	Thermal expansion (ppm/°C)	Young's modulus (GPa)	Data source
Corning	7059	2.76	593	4.6	67.6	Ref. [11]
	1737	2.54	666	3.8	69.6	Ref. [11]
	Eagle XG Slim	2.38	669	3.17	73.6	Catalog
	Lotus XT	2.57	743	3.45	80.7	Catalog
AGC	AN635	2.77	635	4.8	73	Catalog
	AN100	2.51	670	3.8	77	Catalog
	AN-Wizus	2.59	715	3.9	85	Catalog
NEG	OA-2	2.7	650	4.7	75	Catalog
	OA-10	2.5	650	3.8	70	Catalog
	OA-21	2.4	665	3.2	70	Catalog
Avanstrate	NA32SG	2.41	661	3.45	73.9	Catalog

Historically, Corning #7059 glass was the first of such new glass substrates for TFT-LCDs [11]. Currently, Corning, AGC, Nippon Electric Glass, AvanStrate, and LG Chem are other companies that supply such glass substrates for TFT display devices (Table 4). Of particular importance is also a lack of fast-diffusing alkali ions (Chapters 4.2 and 4.3) in the composition. In LCD and OLED panels, the lifetime of TFTs would be shortened through damages caused by alkali intake by diffusion from the glass substrate. Likewise, alkali migration would also impair the electrodes of PDP panels. Alkali-free glasses based on boroaluminosilicate systems are thus commonly used in these cases. Since alkali elements are also the most efficient fluxes to lower liquidus and glass transition temperatures, their removal has in addition helped to improve mechanical properties and minimize thermal compaction during the high-temperature manufacturing steps.

4 Liquid-Crystal Displays

Originally the main limitation of CRTs was the maximum size of about 40 in. of the screens that could be made. As pioneered in the form of monitors in the computer industry, larger screens first relied on liquid-crystal technology, a new development that made use of the unusual optical properties of these phases first discovered in the case of cholesterol derivatives by the Austrian botanist Friedrich Reinitzer (1857–1927) in 1888 in Prague. At Reinitzer's request further observations were then made by Otto Lehman (1855–1922) in Aachen who found that these

crystals reflected circularly polarized light and rotated its polarization direction and also that they exhibited two melting points, first to a cloudy phase and then to a clear liquid. Work then made on the structure and properties of the great many new liquid crystals discovered showed in particular that their phase transitions could be induced by electric fields. These phases remained scientific curiosities, however, because of the temperatures significantly higher than 100 °C at which their phase transitions were taking place.

Display applications of liquid crystals thus awaited the synthesis of liquid crystals undergoing their phase transitions near room temperature. After a first patent for LCD was filed in 1962 in the United States for phase transitions still higher than 100 °C, much work was needed to achieve this goal [12]. Calculators with LCDs were eventually commercialized in 1973 in Japan where they were well received by the market. Another important milestone was the fabrication in Japan in 1984 of portable TVs with color LCDs of 2 in. in size. Thanks to rapid size increases, LCDs could then be used for the monitors of laptop PCs and TVs, while many new technologies were developed to ensure better image quality in particular through a higher resolution, wider viewing angles, and faster response times [13, 14].

In display applications, liquid crystals are either transparent or opaque under cross polarizers depending on the optical properties of the phases in which they have been locked in by an applied electrical field. All pixels are thus driven by distinct electrodes in a few μm thick cells sandwiched between two glass substrates (Figure 7) in which liquid crystals are inserted by vacuum suction. Since

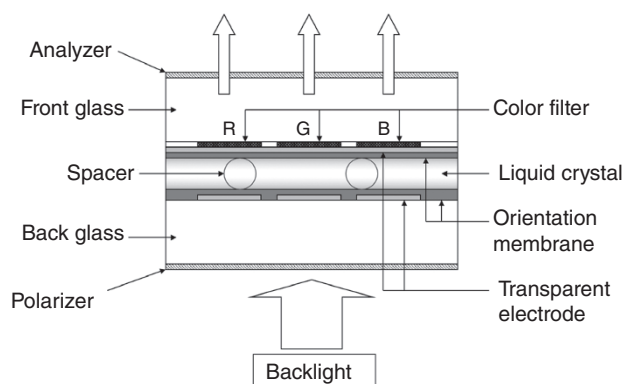


Figure 7 Sketch of a liquid-crystal display. Alkali-free glasses are used for the front and back glasses, and indium-tin oxides for the transparent electrodes. The color filter is formed on the glass substrate from resin and organic or inorganic pigments. Like the liquid crystals, the polarizer, analyzer, orientation membrane, spacer, and liquid crystal are basically made from organic polymer materials.

liquid crystals are not light emissive, the display assembly must include a backlight in addition to the polarizer and analyzer. As the polarization angle of light from the backlight unit is changed by the arrangement of the liquid crystal, the intensity of the light that passes through the analyzer changes, so the brightness of each pixel is controlled. To create a color image, red, green, and blue color filters made of organic resin are formed as alternating vertical bands for each pixel on the front glass substrate. Owing to this complex structure, a low fraction of about 5% of the incident light is actually transmitted.

Many different configurations have been investigated to obtain a high picture quality through high response rates, wide viewing angles, and increased brightness. In an originally common configuration, two linear electrodes placed on the top and bottom of the glass surface create an electric field parallel to the glass plate to drive vertically the liquid-crystal transitions. In the more recent but more expensive *in-plane-switching* configuration, the liquid crystals align horizontally under a lateral electrical field applied between both of their ends to keep them parallel to the electrodes and the glass substrate so that they can move freely without being tied to the surface of the glass.

5 Plasma-Display Panels

The main reason why LCDs initially took over the market was a ready process scalability. But their refreshing rate is limited by relatively low phase transition kinetics, and they also suffer from a restricted contrast due to the

needed backlight, a real black hue being, for instance, impossible to obtain. When large-sized displays attracted a great interest in the late 1990s, it was commonly thought that PDPs were the only alternative because their simple structure was making their fabrication much easier than that of LCDs. Like fluorescent lamps (Chapter 6.9), PDPs rely on the light emitted by noble gases upon electrical discharges. The technology was first demonstrated in the United States in 1962. Applications to TV took a little while to be developed since color PDPs of 20 in. in size were made only in 1987 in Japan where 42 in. color screens then became commercially available in 1996, further efforts having been made to increase the size of TVs and improve their picture quality [15].

In PDPs, two glass substrates are sealed with a gap of about 200 μm (Figure 8) within which an inert gas, typically Xe, is enclosed. Individual pixels are defined by barrier ribs on the inside wall of which phosphors are deposited (Chapter 7.9). The light emitted by xenon is in the ultraviolet range when a discharge occurs between transparent ITO electrodes on the front glass. The function of the red, green, and blue phosphors is thus to emit a fluorescent visible light from the UV radiation of the gas to create a color image.

The dielectric layers and barrier ribs, which compose the unit cell of the PDPs, are formed on the glass substrates from a glass frit sintered at 500–600 $^{\circ}\text{C}$. Therefore, the thermal expansion coefficients of these materials have to match each other. In addition, the stability of the glass substrate against any thermal deformation must be minimized. Although normal soda-lime glass was used as a substrate during the initial stages of color PDPs, special compositions with high strain points have been developed and are now widely used to manufacture large-sized color PDPs (Table 5). These glasses were designed to have a CTE similar to that of soda-lime glass so that the same

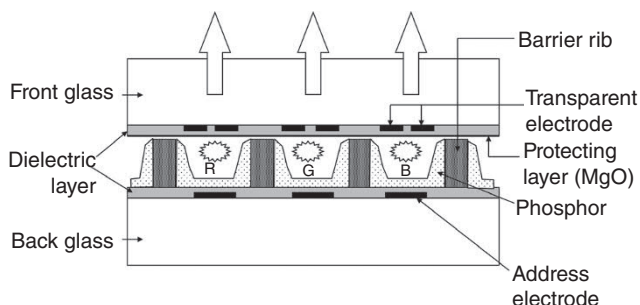


Figure 8 Sketch of a plasma-display panel. High-strain-point glasses are used for the front and back glasses, and sintered glass frits for dielectric layers and barrier ribs. The transparent and address electrodes are usually made from indium-tin oxides and silver, respectively.

Table 5 Properties of glass substrates for plasma-display panels.

Company	Code	Density (g/cm ³)	Strain point (°C)	Thermal expansion (ppm/°C)	Young's modulus (GPa)	Data source
AGC	(Soda-lime glass)	2.49	511	8.5	72	Ref. [12]
	PD200	2.77	570	8.3	76	Ref. [12]
NEG	PP-8	2.82	582	8.3	77	Catalog

frit materials can be adopted. They are currently produced by companies like AGC and Nippon Electric Glass.

Generally, thermal compaction is higher for of PDP than for LCD glass because, as already noted, the process temperature of PDP is closer to the strain point of the material. However, the tolerances are also greater because PDPs are made only in large sizes for which the intrinsic resolution can be lower and, thus, cell sizes be bigger. The mechanical properties of the glass substrate are important issue for PDP as well as for TFT-LCD displays. Thermal shock failure was especially a serious problem in PDP fabrication because the CTE of PDP glass is much higher than that of TFT-LCD glass and also because the substrate is exposed many times to high temperatures [16].

6 Organic Light-Emitting Diodes

With respect to solid-state inorganic LEDs, OLEDs have the big advantage of making use of transparent semiconducting organic liquids, which makes in principle production of large light-emitting surfaces easy (Chapter 6.9). For display applications, additional advantages are high contrast and refreshing rates, thinner devices due to the need for single glass panel, and high energy efficiency because only the lit pixels consume energy. In 1987, a prototype OLED display was first demonstrated in the United States [17]. As early as 1997 a monochromatic OLED device was installed in car audio systems in Japan. In early 2000, color OLED devices began to be used for mobile displays such as smartphones. In contrast to LCDs, however, production scalability was not ready for OLED displays because of deposition and patterning difficulties. Commercial production of OLED TVs nonetheless began in 2007 with 11 in. screens in Japan. Since then, large-sized and high-resolution OLED TVs have been developed [18] and now strongly compete with LCD TVs in the market.

As described in more detail in Chapter 6.9, the main components of an OLED are a hole-injecting anode, the organic light emitter, an electron transportation layer,

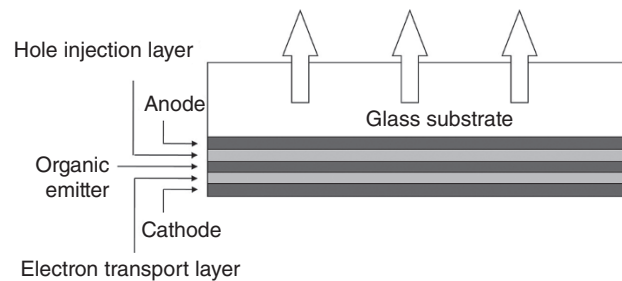


Figure 9 Sketch of an organic light-emitting diode. Transparent electrode (ITO) and organic components deposited and patterned on the alkali-free glass substrate.

and an electron-injecting cathode deposited on the glass substrate (Figure 9). When a voltage is applied between the anode and cathode, holes and electrons are transferred to the organic layer where they form excitons that emit light when relaxing to the ground state of the valence band. Because OLEDs are driven by TFTs, substrates are basically made up of the same alkali-free glasses as those of LCDs. After all materials are deposited and patterned to make pixels on the glass substrate, they need to be encapsulated to be protected from moisture or oxygen attacks because most of organic materials in OLED devices are very weak against those gases.

7 Device Configuration

As illustrated by a smartphone configuration (Figure 1), many glass substrates having each function are combined in actual devices using FPDs. In LCDs, for example, a clear glass plate for guiding the backlight is used in addition to the front and back glasses. In all devices, a transparent touch sensor for human interfacing is now essential. In both the *resistive* and the *projective capacitive* touch sensors, which are two major technologies commonly used for handheld devices, glass is once more a fundamental element on which either electrodes or insulators are deposited, whose signal is then analyzed to locate the point of the screen that has been selected

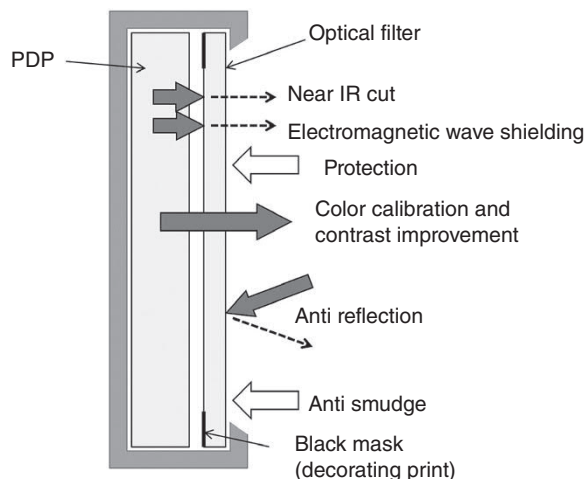


Figure 10 Functions of the optical filter of a plasma-display panel.

by the user. And, as already described, the surface of the device is protected by a chemically tempered cover glass.

Finally, a few words must also be said about the typical optical filters used in PDP TVs (Figure 10). Their main purposes are (i) to calibrate color and (ii) to improve contrast. But they have many other functions, namely, (iii) to cut near-IR radiation to avoid interferences with other remote control units, (iv) to shield electromagnetic waves, (v) to be an antireflective layer (Chapter 6.8), (vi) to protect the panel from mechanical damage such as caused by impact, and (vii) to prevent smudge. Within the filter glass, a black mask is sometimes applied for decoration. Soda-lime glasses with some coatings and films are generally used to provide these functions.

8 Perspectives

The extremely strong and rapid decline of CRTs was not anticipated at all when flat displays appeared on the market in the late 1990s. Rather, it was thought that glass recycling would be the main issue [19, 20] to be solved adequately to keep their production going on. Likewise, the development of OLEDs has been much faster than expected. But it must also be stressed that all advances made in the last decades to switch from analog to digital image transmission would have been impossible without the availability of fast and cheap microprocessors and controllers to activate pixels whose numbers reach millions in the largest displays.

The size of current displays is now so large, and their resolution is so good that little room might seem to be left for real improvements in these respects. Building on the idea implemented in shopping malls or stadiums of giant displays made with usual LEDs, work is nonetheless done

to develop displays with pixel-sized, GaN-based micro-LEDs. The advantages would be a simpler structure (substrate, electrode, microLEDs, glass cover) and thus reduced thickness and weight, combined with further improvements in brightness, response times, energy efficiency, and lifetime, which would make these new displays especially valuable for smartphones or watches.

Guessing what additional advances might be made afterward is difficult. Since LEDs have been the last known source of light remaining to be exploited, some time will likely elapse before new devices are designed on a completely new basis. As illustrated by the *wind-screen* of cars (Chapter 9.2), a current trend is rather to include displays in an ever greater variety of devices and of settings. Another striking feature of the electronic revolution actually is the convergence that is making irrelevant to keep fundamental distinctions between TV sets, telephones, or cameras. Whether large or small, displays will thus be playing a fundamental role in all cases.

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**Encyclopedia of Glass Science,
Technology, History, and Culture**

Encyclopedia of Glass Science, Technology, History, and Culture

Volume II

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– 8.6: Relaxation Processes in Molecular Liquids.

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– 6.5: Fluoride and Chalcogenide Glasses for
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– 6.2: The Color of Glass.

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– 9.9: Glass Cullet: Sources, Uses, and Environmental Benefits.

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– 10.6: Glazes and Enamels.

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– 7.11: Glass-Ceramics.

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– 1.2: Raw Materials for Glass Making: Properties and Constraints.

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– 5.7: Optical Basicity: Theory and Application.

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– 2.5: The Extended Structure of Glass.

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– 3.3: The Glass Transition and the Entropy Crisis.

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– 4.6: Atomistic Simulations of Transport Properties.

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– 2.3: Microstructure Analysis of Glasses and Glass Ceramics.

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– 4.5: Thermal Diffusivity and Conductivity of Glasses and Melts.

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– 9.7: Design and Operation of Glass Furnaces.

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– 8.1: Biogenic Silica Glasses.

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– 9.1: Structural Glass in Architecture.

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Preface



When art meets glassmaking: the visit of the Duchess of Berry (1798–1870) in 1824 to the plate-glass factory of the Royal Manufacture of Saint-Gobain as depicted by Édouard Pingret (1788–1869). The stifling heat, the noise of the furnaces, and the danger for the workers of the molten glass poured from the pot and spread with the steel roller on the large table (Chapter 10.9) have all vanished. Only the theatrical aspect of the scene remains, highlighted by the tall curtain, the duchess's light-colored dress echoing the worker's white smocks, and the children watching the show from the balcony. *Source:* Photo courtesy Saint-Gobain Archives.

The *Encyclopedia* has been designed to satisfy the needs and curiosity of a broad audience interested in the nature, properties, fabrication, and history of glass and looking for consistent, comprehensive, and up-to-date information in a single book. More than 100 chapters involving even more glass experts have been written in a perspective that combines the various aspects of this unique material, be they scientific, technological, industrial, historical, or cultural. Whether coming from academia or industry, the authors have in common a long practice of glass. Their goal is to be informative without being pedantic, to be concrete without being boring, and to give a balanced overview of the field – in a word, to allow a large readership to understand both the amazing properties of the vitreous state and its peculiarities compared with those of other states of matter. Excluding the so-called spin glasses and other kinds of disordered physical systems, the *Encyclopedia* restricts itself to what is now termed *structural* glass.

In all chapters, the authors discuss glass from a materials-science standpoint, but their purpose is not to review in any detail the latest advances of interest to specialists only. Rather, in the form of scholarly introductions, it is to present every topic at a uniform level and in a self-consistent manner. In this way, the main points will be grasped and key information of fundamental or practical use will be made available. The neophyte reader will then be able to consult the specialized literature and, in particular, the select bibliography appended to each chapter.

This approach does not imply that only elementary features are presented, but that concepts are appropriately introduced and any technical information clearly explained so as to avoid the common defect underlined in 1911 by the astronomer Percival Lowell (1855–1916) who emphasized in *Mars and its Canals* that “nothing in any branch of science is so little known as its articulation, — how the skeleton of it is put together, and what may be the mode of attachment of its muscles.” Whereas a very few chapters give a flavor of current technicalities involved in glass research, newly investigated topics are also considered with the goal of ensuring that the *Encyclopedia* remains a useful reference over an extended period of time. Although those views that are at this moment very speculative are generally not discussed at length, they may be stated in the final *Perspectives* of the chapters.

Given the diversity of topics treated, the name of *Encyclopedia* (*Kuklos paideia*, cycle of enlightenments, in Greek) is particularly appropriate. The surprising fact is that such a reference work was not existing at all for glass, in general, even though more than hundreds of thousands of encyclopedias have now been devoted to any topic worth of attention, including glass art in particular. The

Encyclopedia consists of 10 sections preceded by a general introduction and concluded by a postface. It begins with glassmaking and continues with structural, physical, and chemical properties. The stage is then set to turn to issues pertaining to light, to the main inorganic glass families, to organically related glasses, to environmental and other industrial issues, and, finally, to the main facets of the rich glass history. Even in more than 100 chapters, it has not been possible to deal with every important topic relevant to glass. A few more chapters would have been welcomed, but their advantages would not have outweighed the inconvenience of a longer publication time, especially for the *Encyclopedia* contributors.

Each section is preceded by a short introduction summarizing in a few sentences the contents of its chapters for helping readers to decide which ones fit their own interest best. Another purpose of these introductions is to show that, from the first to the last, the chapters are telling a consistent story. Although efforts have been made to avoid overlap, some limited duplication was inevitable to make sure that most contributions could be read independently of the others. Of course, boundaries between chapters or sections are not always clear-cut, so that some arbitrariness has been involved in their delineation. And whereas the scientific and technology contents of the chapters will probably speak for themselves, it might be useful to note that historical aspects are dealt with not only in the last section but also elsewhere each time they can help to open deeper perspectives. As for the *Culture* included in the title of the *Encyclopedia*, it is explicitly treated only in the very last chapter but pervades a great many others, for example, in the history section where beautiful pieces of art are in particular reproduced.

At the end of this endeavor, it is now a pleasure to acknowledge (i) the encouragement initially provided by R. Conradt, N.G. Greaves, J. Livage, J. Lucas, B. Mysen, A. Takada, and Y. Yue when the project took shape; (ii) the warm welcome this project received through G. Geiger and A. Lekhwani when submitted to the American Ceramic Society and John Wiley & Sons; (iii) the invaluable help then brought all the way by Reinhard Conradt and Akira Takada through their constant advice, support, friendship, and careful reviewing work; (iv) the great many graphics and pictures neatly prepared by Joël Dyon to highlight the matter presented in numerous chapters; (v) the efforts of 151 authors working in 23 countries who participated in this ambitious endeavor and went responsively throughout an editorial process aimed at ensuring an overall homogeneity of style and content, and incorporated in their texts the relevant historical and cultural aspects evoked by the *Encyclopedia* title; (vi) the thoughtful comments and apt observations provided

by nearly 200 reviewers whose names are included at the beginning of every chapter to recognize publicly their contributions; (vii) the original pictures or help in different matters generously provided by colleagues, friends, and institutions whose names are mentioned at the relevant places; (viii) the Humboldt Stiftung, the Ludwig-Maximilians-Universität, and Donald Dingwell for the fruitful work done in Munich; (ix) the so many things about glass or high-temperature techniques and processes discussed over the years with T. Atake, J.-L. Bernard, Y. Bottinga, R. Conradt, K.-U. Hess, R. Kerner, B. Mysen, G. Ottonello, J.-P. Petitot, J. Roux, A. Sipp, J.F. Stebbins, A. Takada, C. Téqui, and other colleagues too numerous to be mentioned; (x) the Table of ion data compiled by J.F. Stebbins, the help provided at various stages of this study by É. Fareau, B. Gasparyan, K.-U. Hess, A. Hofmeister, K. Meliksetian, B. Mysen, and M. Wolf as well as thoughtful comments by J.M. Parker and R.F. Tournier on the section introductions; (xi) and finally Michael Leventhal who oversaw the project at Wiley, Stefanie Volk for copy editing and Viniprammia Premkumar for smooth and responsive production of the book.

The *Encyclopedia* is dedicated to them and to all people whose efforts throughout the ages made glass the astonishing, ubiquitous material it has become.

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Section VII. Inorganic Glass Families

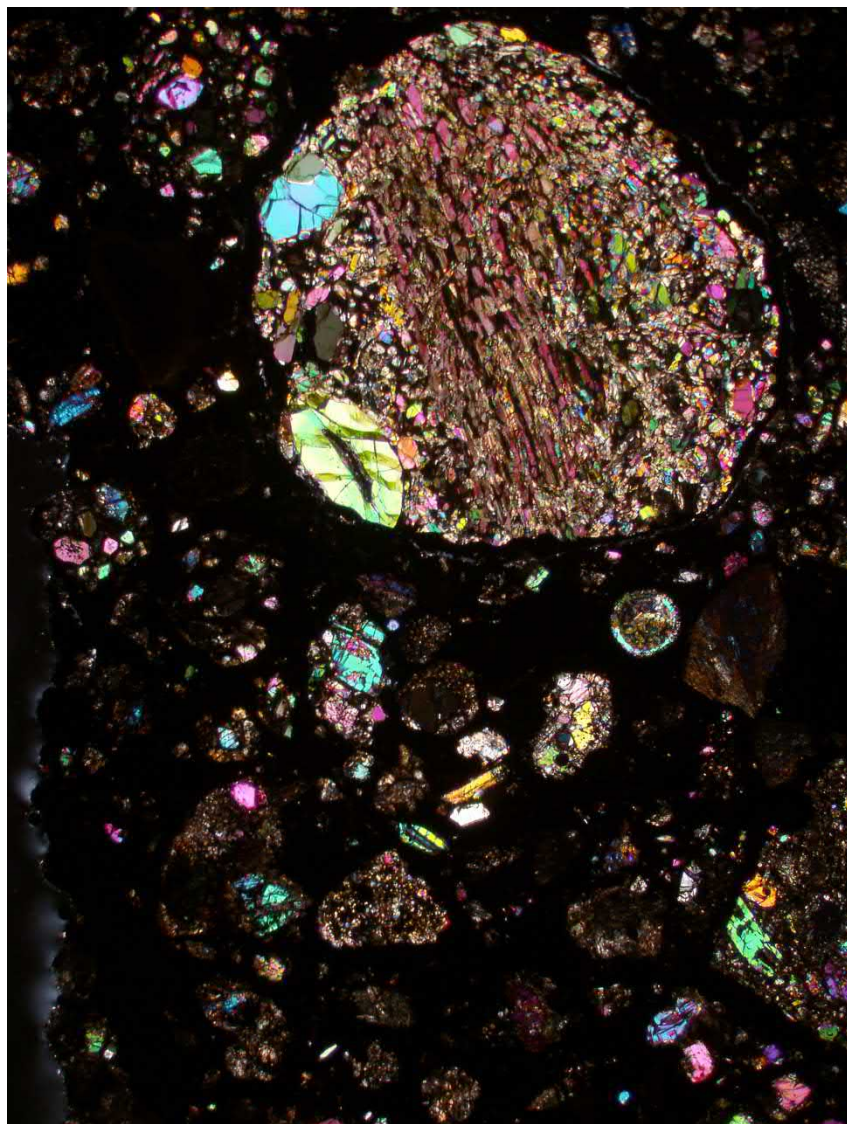


Figure 1 The oldest known glass phases, dating back to the beginnings of the solar system: the 4.57-billion-year-old matrix (dark black) of *chondrite* meteorites, which owe their names to their spherical *chondrules*. Shown here is a big one of 3 mm in size made up of a highly birefringent, rapidly quenched olivine crystal [(Fe,Mg)SiO₄]. Thin section of Chainpur chondrite, which fell in 1907 in India. Optical micrograph under polarized light by Maxime Bronchy, courtesy François Robert, MNHN, Paris.

Inorganic glasses are as old as the first planetary bodies, which probably began to form by accretion of celestial dust very long before the birth of the solar system 4.57 billion years ago. As indicated by the amorphous *mesostasis* of certain meteorites (Figure 1), this was the time when the oldest known glasses were quenched from the high-temperature accretion conditions prevailing in *protoplanets*. Extraterrestrial glasses have then variously resulted from volcanic planetary activity, the effects of high-pressure impacts, and irradiation or friction upon entry of cometary or asteroidal material into the Earth's upper atmosphere. These processes are described in the first chapter of this section by G. Libourel who also explains how important information on the early history of the solar system can be derived from studies of these different kinds of glasses (Chapter 7.1).

On Earth, too, glasses formed very early. In contrast to the almost infinite metastability enjoyed under high vacuum by their extraterrestrial counterparts, they suffer more or less rapidly from weathering by aqueous solutions. They exhibit widely differing compositions, which translate into very large viscosity increases at magmatic temperatures from SiO_2 -poor to SiO_2 -rich lavas; eruptive styles vary accordingly from gentle to violently explosive and in productions ranging from aerodynamically drawn glass fibers to massive obsidian blocks. These effects are discussed by C. De Campos and K. Hess in the chapter devoted to natural glasses, which also deals with fulgurites, formed by lightning, as well as tektites and silica Libyan Desert glass whose formation is induced by the fall of cometary or meteorite impacts (Chapter 7.2). Because most fresh lavas erupt on Earth along the extensive mid-ocean ridges, very large amounts of glass form upon quenching by seawater under conditions that are, therefore, prone to rapid corrosion. As described by R. Hellmann, the mechanisms of both biotic and abiotic processes at work have been largely deciphered and appear to play a considerable role in the global geochemical cycles of chemical elements (Chapter 7.3).

The rest of this section is devoted to man-made glasses. In metallurgy, 400 million tons of Ca-rich slags yearly produced are closely related to natural glasses because they originate in the melting of ores in blast furnaces where metal oxides are reduced by reaction with coke. Owing to their low SiO_2 contents, slags are very fluid and have a high electrical conductivity. These properties reviewed by K.C. Mills play a critical part in the kinetics of metal processing; as a result of a strong chemical affinity for impurities, slags in addition concentrate sulfur and phosphorus, which would have deleterious effects on metal properties (Chapter 7.4). The so-called water glasses are also SiO_2 poor but alkali rich and are named after their high solubilities in aqueous solutions. These features discussed by H. Roggendorf make them valuable as highly reactive sources of silica and alkalis, or as precursors in silicate synthesis, in the form of monomeric or polymeric species in

concentrated aqueous solutions (Chapter 7.5). On the contrary, borosilicate glasses are extremely stable in aqueous solutions; in addition, they are easily melted and exhibit unusually low thermal expansion. As described by R.E. Youngman, these features result from the very low melting temperature of 712 K of B_2O_3 along with mixing of B^{3+} and Si^{4+} in the anionic framework made possible by association of boron with charge-compensating cations; the entropy of Si-B mixing thus enhances the depressing effects of B_2O_3 on liquidus temperatures without affecting the polymerization state and stability of the material (Chapter 7.6). Since a low reactivity with aqueous solutions and other liquids is a prerequisite in pharmacy, borosilicates are the prime glass containers in this domain although chemical processes such as ion exchange, silicization, or reaction with ammonium sulfide presented by D. Zuccato and E. Guadagnino can increase the hydrolytic resistance of usual container glass for less demanding applications (Chapter 7.7).

The next three chapters are devoted to not-so-well known families of glasses. First, oxynitrides owe their name to the large amounts of nitrogen that can be chemically dissolved in a rather wide range of silicate compositions; S. Hampshire and M. Pomeroy document why their network is rigidified when oxygens are substituted by cross-linking nitrogens and, thus, why they display improved mechanical properties (Chapter 7.8). With widely differing PO_4 chain structures, the phosphate glasses addressed by A. Parsons distinguish themselves by their ability to accommodate large concentrations of a great many modifier oxides, which has resulted in a variety of applications ranging from baking powder and *phosphors* to nuclear waste storage and high power lasers (Chapter 7.9). Although they were first produced as ribbons only in the 1960s, metallic glasses constitute a very rapidly developing family, which combines the traditional advantages of metals and glasses with regard to mechanical, magnetic, and molding properties. Owing to the poor vitrifiability of metals, the main difficulty encountered was to increase the size of the glass pieces obtained in the bulk. As explained by D. Louzguin-Luzgin and A. Inoue, the solution was to turn to multicomponent systems so as to take advantage of smaller intervals between liquidus and glass transition temperatures and make crystal nucleation and growth more difficult (Chapter 7.10).

The last chapter is devoted to partially crystallized glasses known as *glass ceramics* whose practical applications range from familiar cooktop panels to large telescope mirrors. The main features presented by M. Comte are thus the way in which their microstructure is engineered by appropriate choices of chemical composition, nucleating agents and heat treatments to grow, directly or after phase separation, and the desired crystalline phases that will confer outstanding chemical or thermal shock resistance to the resulting composite material, which may even be transparent (Chapter 7.11).

7.1

Extraterrestrial Glasses

Guy Libourel

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1 Introduction

After four millennia of observations of the sky made with the naked eye, glass led Galileo (1564–1642) and his followers to discover a whole new celestial world through the lenses of their telescopes and to change accordingly man's worldview (cf. Chapter 10.10). To observe the universe still farther and in more detail, the need to increase the size of telescopes was clearly realized in the eighteenth century. Astronomy did not greatly benefit from the important advances made in the making of optical glass (Chapter 10.10); however, because reflecting telescopes (with metallic mirrors) then had the major advantage over refracting instruments of not been subject to chromatic aberration so that the only glass part was the eyepiece. In England, the German-born musician William Herschel (1738–1822) was at the forefront of these efforts not only as an observer and a theoretician but also as a mirror grinder and a telescope maker. Whereas about 100 nebulae were known when he began his observations, he described himself 2500 nebulae and star clusters in a series of papers devoted to the “Construction of the heavens” [1]. These observations of new worlds in the making quickly served as the basis of the theory propounded by Pierre-Simon de Laplace (1749–1827) to explain how all planets formed by condensation of interstellar dust and why they were orbiting in nearly the same plane and in the same direction in the Solar System [2].

But the chemical composition of the dust and the processes that formed planets orbiting around a star of course had to be determined. In this respect, a fundamental observation also made at the beginning of the

nineteenth century was that meteorites were fragments of heavenly bodies. That these objects were either stony or metallic (or both for a few of them), was especially striking as the Earth itself was later thought of consisting of a metallic core surrounded by a large silicate envelope. The relevance of meteorites to planetary studies was soon ascertained by the idea that these objects were fragmented remnants of planetesimals, the stable bodies larger than about 1 km resulting from the early accretion of dust, ice, and rocks in the protoplanetary disk. More recently, other kinds of extraterrestrial materials have been recovered. Millimeter-sized micrometeorites and interplanetary dust particles have been collected from the Earth's stratosphere to oceanic sediments whereas other samples have been brought back by space missions sent to the Moon (Apollo and Luna), a near-Earth asteroid named (25143) Itokawa (Hayabusa), a comet dubbed 81P/Wild (Stardust), and through the solar wind (Genesis).

Of particular interest is the glass phases found in these materials because they reveal the existence of melting stages in the planetary formation or activity and can even yield information on their kinetics. In contrast to most of their Earth counterparts, however, extraterrestrial glasses have generally encountered very peculiar and sometimes highly disequilibrium conditions, for instance, microgravity and high vacuum, high-velocity impacts, solar-wind irradiation, or extremely reduced environments caused by elevated carbon/oxygen ratios within the solar nebula. These extraterrestrial materials are thus of key importance not so much for inventorying the celestial bodies constituting the Solar System, but rather for understanding its formation and evolution since its birth.

Here, three different kinds of extraterrestrial matter will be described to illustrate the kind of conclusions that can be drawn from their studies. First, *chondrites*, the most primitive type of meteorites, show how

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extraterrestrial glass allows one to see far back in time for understanding the composition and evolution of the disk in terms of events, such as condensation of hot gases or transient heating caused by the formation of the Sun, whose mechanisms and timing must be determined [3]. Second, lunar glasses demonstrate the existence of two quite different glassmaking processes, the first extinct in the form of volcanic eruptions and the second still active through micrometeorite bombardment. Finally, small glass spherules found in special environments reveal that the Earth's surface is also continuously sprinkled by micrometeorites that reach the ground into a more or less preserved condition. A few implications of these results for cosmochemistry and glass science will finally be described.

2 Chondrules: The Oldest Glasses of the Solar System

Chondrites are stones representing about 85% of known meteorites. They are the oldest objects known to man because they formed right at the same time as the Solar System (Figure 1). They owe their name to their *chondrules* (*khondros*, small grain in Greek), the small spherical glass-rich inclusions that give them unique textures. In addition to chondrules, chondrites contain 10–15 vol % of refractory calcium–aluminum-rich inclusions (CAI), which were the first solids to condense at close heliocentric distances of 0.1 astronomical unit (1 AU $\approx$ 1.5 10^8 km, the mean Earth–Sun distance) out of a hot gaseous nebula [4]. As dated from the decay of ^{235}U (half-life of $0.71 \cdot 10^9$ years) and ^{238}U ($4.56 \cdot 10^9$ years), these

inclusions condensed 4567.30 ± 0.16 million years (My) ago [5], which represents our current best estimate of the age of the whole Solar System. Chondrules have the same age or may be slightly younger by up to 2–3 My [5].

Depending on chemical and mineral compositions, these meteorites are generally split into three main types, namely ordinary, carbonaceous, and enstatite (MgSiO_3 pyroxene rich) chondrites. Constituting up to 80% of their volumes, chondrules [6] are submillimeter- to millimeter-sized spherules in which a glass matrix coexists with olivines $[(\text{Mg,Fe})\text{SiO}_4]$, pyroxenes $[(\text{Mg,Fe,Ca})_2\text{Si}_2\text{O}_6]$, Fe–Ni metal, and sulfides like troilite (FeS) or oldhamite $[(\text{Ca,Mg})\text{S}]$. In view of large variations in bulk chemical composition, they are classified further into FeO-rich, FeO-poor, and Al-rich chondrules. In most chondrite groups, FeO-poor chondrules (type I) are dominant; on the other hand, Fe^{3+} -bearing chondrules (type II) are abundant only in ordinary chondrites, whereas Al-rich ones are scarce in all.

The glassy matrices display concomitantly large compositional variations (Table 1) since the SiO_2 content ranges from 40 to 85 wt % with a negative correlation with Al_2O_3 , CaO , and TiO_2 contents [7]. They display a wide variety of textures (Figure 2), some of which represent strong evidence for extremely rapid cooling from a molten or nearly completely molten state. In rare cases, they are entirely composed of glass, suggesting an even faster quenching. Other features that are clearly the result of very rapid cooling are dendritic and hopper-shaped crystals in a glassy matrix (Figure 2). But the most frequent texture is said to be *porphyritic*, meaning that some crystals are much larger than others, either olivines or pyroxenes, or both. Owing to the kinetics of crystal growth (Chapter 5.4), these chondrules likely cooled more slowly than those with radial or barred textures although they still may have solidified in a matter of hours.

From these observations and experimental work aiming at reproducing textures [10], it has been concluded that chondrules were produced by brief, incomplete melting (from about 1600 to 2000 K) of solid dust precursors in the solar protoplanetary disk (Figure 3). It also appears that chondrules solidified as melt droplets freely floating in space before being aggregated into the chondrite parent bodies [11]. The heat source that caused melting in the solar protoplanetary disk has not been unambiguously identified, however [5, 11]. The astrophysical or planetary origin of this source involved is still debated. Among possible processes are solar nebula lightning, nebular shocks driven by eccentric planetesimals, nebular shocks driven by disk-wide gravitational instabilities, or a sudden exposure to sunlight at distances smaller than 0.1 AU from the protosun, with subsequent launching in a magnetocentrifugal outflow (the so-called X-wind model).

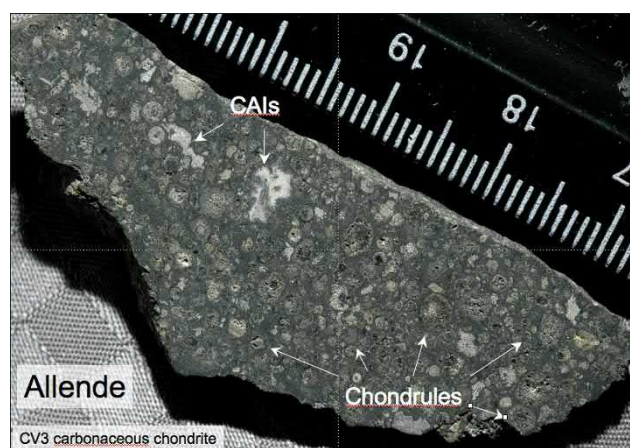


Figure 1 Ferromagnesian chondrules and calcium, aluminum-rich inclusions cemented by a fine-grained matrix in the Allende CV3 carbonaceous chondrite. With more than 2 tons of fragments recovered, Allende is the biggest carbonaceous chondrite known so far. It fell on 8 February 1969 near Pueblito de Allende in Mexico.

Table 1 Extraterrestrial glass compositions.

Chondrules	FeO-poor type I					FeO-rich type II		Al-rich
	PO	POP			PP	PO	POP	PO
	Core	Rim	Melt inclusions			Core	Rim	Core
SiO ₂	46.00	56.80	40.50	58.58	64.96	62.15	63.80	47.02
TiO ₂	1.30	0.32	1.20	0.43	0.35	0.39	0.52	1.03
Al ₂ O ₃	25.70	22.10	28.30	19.47	18.23	10.18	13.56	24.23
Cr ₂ O ₃	0.24	0.18	0.22	0.25	0.08	0.12	0.01	0.17
FeO	0.19	0.39	0.34	0.84	0.43	10.29	6.52	0.17
MnO	<0.07	0.26	<0.07	0.38	0.42	0.32	0.28	0.08
MgO	5.40	3.50	4.10	3.47	1.87	2.29	1.34	5.95
CaO	19.20	10.90	22.60	9.53	3.75	4.25	1.83	18.76
Na ₂ O	0.23	5.40	0.75	6.37	6.88	6.62	9.09	0.29
K ₂ O	<0.04	0.27	<0.04	0.38	0.83	0.68	0.87	0.01
Total	98.30	100.20	98.00	99.71	97.80	97.27	97.80	97.70
Lunar glass	Green	Green	Yellow	Brown	Orange	Red	Red/brown	Dark
	15401,27	15427	15427	15425,26	Apollo 15	Apollo 15	15427	Apollo 15
SiO ₂	45.30	45.20	42.47	42.86	37.90	35.60	36.16	34.00
TiO ₂	0.40	0.35	3.96	3.58	9.12	13.80	13.48	16.14
Al ₂ O ₃	7.52	7.73	9.81	8.48	5.63	7.15	8.54	4.60
FeO	20.00	19.77	21.78	21.97	23.70	21.90	20.48	24.50
MnO	0.22	0.31	0.22	0.32	–	0.25	–	0.31
MgO	17.10	16.66	12.39	12.63	14.90	12.10	10.45	13.30
CaO	8.43	8.42	9.23	8.40	7.41	7.89	8.89	6.90
Na ₂ O	0.13	0.22	0.53	0.36	0.36	0.49	0.64	0.23
K ₂ O	<0.06	0.07	0.45	0.09	–	0.12	0.50	0.16
Total	99.10	98.73	100.84	98.69	99.02	99.30	99.14	100.14
Cosmic spherules	Black	Dark green	Dark brown	Black	Dark green	Pale green	Pale green	Black
	Norm	Norm	Norm	Norm	Norm	CAT	CAT	Ca-Al
	7b-125	7b-57	19b-04	7b-127	18c-17	7b-55	7b-54	21p-02
SiO ₂	44.52	47.20	52.20	53.70	56.40	42.10	54.50	48.80
TiO ₂	0.25	0.22	0.15	0.09	0.15	0.38	0.16	0.44
Al ₂ O ₃	2.74	4.31	3.55	0.74	3.49	8.43	3.15	12.10
FeO	8.33	7.25	10.50	15.90	9.22	2.89	2.17	11.90
MnO	0.16	0.19	0.39	0.60	0.55	0.16	0.15	0.26
MgO	42.00	37.90	29.30	27.00	28.20	39.80	38.10	20.50
CaO	2.41	3.62	4.20	1.55	2.42	6.77	2.50	5.27
Na ₂ O	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
K ₂ O	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total	100.40	100.80	100.20	99.80	100.40	100.50	100.70	100.70

Chondrules of Semarkona 3.0 ordinary chondrites [7]; Lunar glass beads from Apollo 15 sites [8] and cosmic spherules from Transantarctic Mountain micrometeorite collection [9].

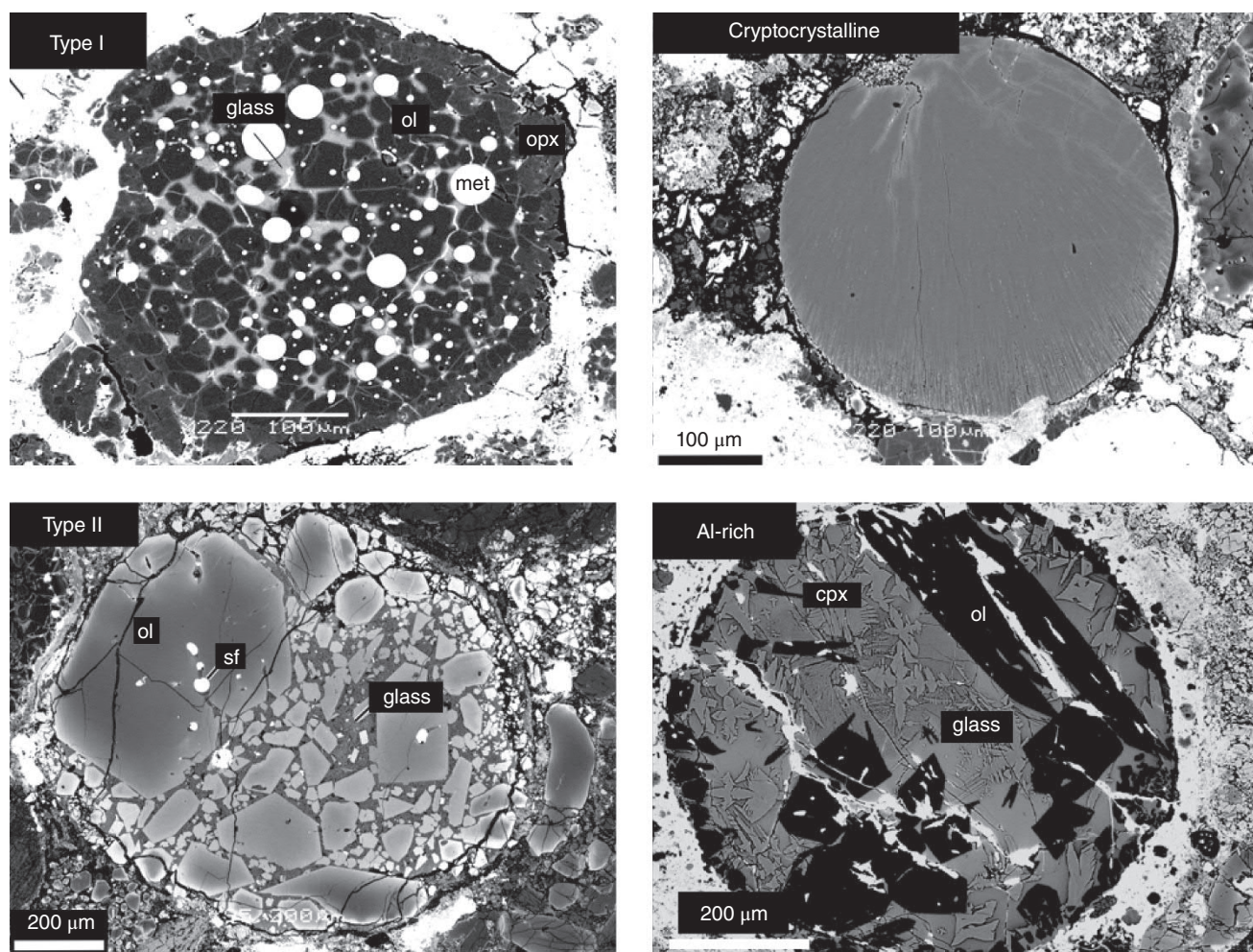


Figure 2 Within glassy matrices, the varying textures of chondrules in the Semarkona LL3.0 unshocked unequilibrated ordinary chondrite (1940 fall in India).

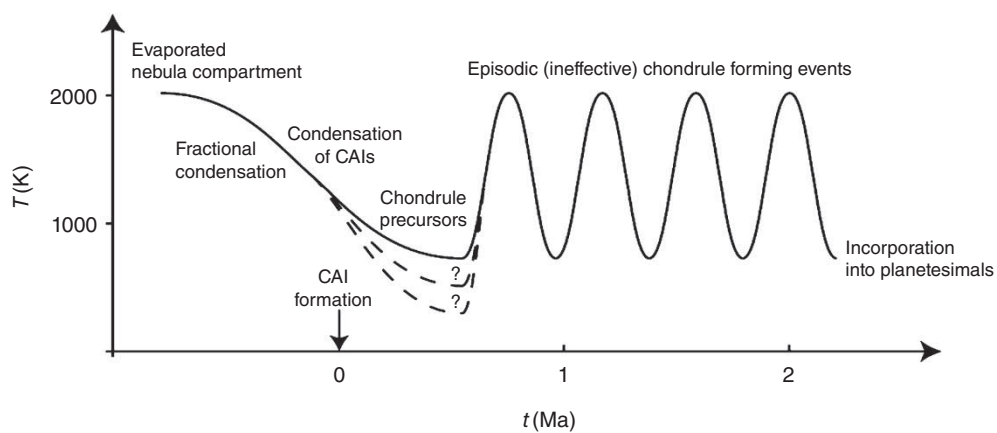


Figure 3 Time-temperature pathway for the formation of chondrules and calcium, aluminum-rich inclusions from D. Hezel (pers. communication).

Experimental studies of chondrule melting and partial crystallization do allow chondrule formation models to be tested [12]. Specifically, chondrule textures are duplicated in dynamic crystallization experiments from peak temperatures from about 1600 to 2000 K at cooling rates ranging from 10^3 to 10 K/h [10]. These results strongly favor large-scale shocks driven by gravitational instabilities or possibly bow shocks driven by planetesimals on eccentric orbits [12]. Primordial dusty materials would have thus been flash-heated from less than 650 K to well above the liquidus (i.e. 1600–2000 K) and then cooled at elevated rates of the order of 10^4 – 10^3 K/h that would have slowed down to the 10^3 – 10 K/h range depending on the optical depth or dust/gas ratio of the medium. For a given chondrule, heating from the peak temperature and cooling down to the glass transition temperature (T_g) depending on the cooling rate would have lasted from hours to several tens of hours for the slowest cooling rates.

The nature of chondrule precursors is also a key question. Did chondrules form from condensate dust or liquid condensates from the nebula gas, from the recycling of previous generations of chondrules or chondrule-like materials, or from disrupted primordial planetesimals? [7, 10, 11]. As discussed since the early 1970s, another important problem is whether moderately volatile elements present such as Na or K have been lost by evaporation or gained by condensation from the gaseous environment during chondrule-forming events [7]. Central to this issue are gas compositions and dust densities in the surroundings of chondrules. How so much dust could have concentrated in at least some places in the solar nebula and how non-nebular gas much enriched in volatile and moderately volatile elements could have been produced? Clearly, more theoretical work is needed to answer such questions.

Whereas chondrules are ubiquitous in almost all chondrite groups, their formation thus remains an enigmatic process. Many melting mechanisms have been put forward over the last decades to explain their igneous textures. One idea is that shock waves sent in by spiral waves in an asymmetrical disk or generated by large planetesimals passing through the dust-rich region heated and melted the starting materials of the chondrules. Other alternatives, such as an impact on molten or partially molten planetesimals, would also work for chondrule formation but need to be investigated. Quoting Alexander and Ebel [11], one may still wonder whether it will be possible to solve the apparent contradictions between the petrologic, isotopic, thermodynamic, and astrophysical constraints on chondrule formation.

3 The Lunar Glass-Bead Factory

3.1 Volcanic Glasses

Herschel himself believed to have observed volcanic eruptions on the Moon [13]. Although he was clearly mistaken on this count, extinct lunar volcanism has been well documented by samples brought back by Space missions. According to radiometric dating, the Moon formed ~ 4.5 billion years ago, about 30–100 million years after the Solar System [14], likely from the matter ejected into an Earth-orbiting disk after a massive, off-center collision of the proto-Earth with a smaller planet [15, 16]. The Moon had a mass large enough to have gone through an Earth-like geochemical differentiation into a metallic core and silicate mantle and crust. Its surface geology is dominated by alternation of lunar plains (*mare*, seas), e.g. some vast solidified pools of ancient iron-rich basaltic lava mainly found on the near side, and lunar highlands on the far side consisting of rocks named anorthosites, i.e. plagioclase feldspar cumulates, which are interpreted as the precipitated remnants of a wide lunar magma ocean.

Highland terrains are on the average older (4 and 3.85 billion years) than the mare where the majority of basaltic eruptions occurred from 3.5 to 3 billion years ago. The other major geologic process that has been affecting the Moon's surface is impact cratering caused by asteroid and meteorite bombardment. Through impact repetition, the outermost crust of the Moon is highly comminuted in the form of a *regolith* (*rhēgos*, blanket, *lithos*, rock), a layer of fine-grained particles and impact debris. As may be expected, the regolith is thicker on older highlands (~ 10 m) than on younger mare (~ 5 m), but in both instances it remains slowly stirred and mixed by new impacts. Figuratively termed *impact gardening*, this process is largely due to micrometeorites, which, thanks to the lack of an atmosphere, can reach the ground and affect its first few millimeters.

Samples of the lunar regolith include breccia and rock fragments from the local bedrock. They are fine grained with a density of ~ 1.5 g/cm³ and a particle size of less than 60–80 μ m for about half of their mass. A variety of colorful volcanic glasses (Figure 4) have also been found in the form of green spherules at the Apollo 15 site and of orange and brown spherules, along with black beads at the Apollo 17 site [17]. The orange glasses owe their unusual hue to high TiO₂ contents of up to about 16 wt % (Chapter 6.2), whereas the beads are black because of the presence of many tiny ilmenite (FeTiO₃) crystals on the olivine blade margins. These features are typical of lava fountain eruptions, possibly several days or weeks long, during which liquid droplets vitrified upon quenching when falling from

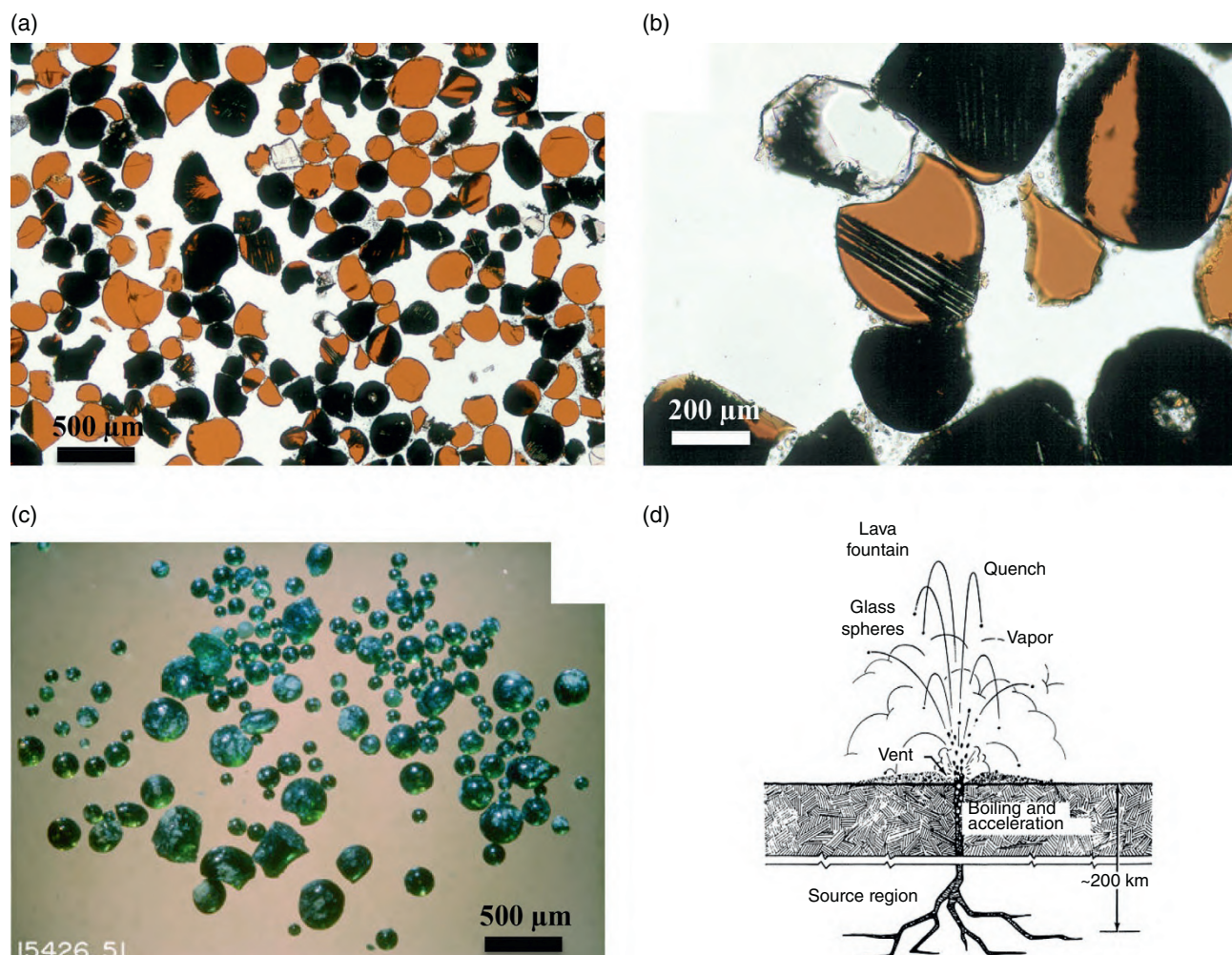


Figure 4 Lunar colorful glass beads collected by the Apollo 15 and 17 missions. (a) Quenched fire-fountain droplets of erupting high-Ti mare basalt dated at 3.48 Ga: sample made mostly of orange, fractured, and partially devitrified glass sphere with a small admixture of mare basalt fragments. (b) Close-up of some spheres, showing one (center) with four long olivine blades that grew from lower right to upper left; the black margins (tiny ilmenite crystals) can be differentiated from the colorless olivine in the blades. (c) Green glass beads of 40–250 μm size in the lunar sample 15426 collected by the Apollo 15 mission. (d) Sketch of a hypothetical lunar volcanic vent and fire fountain producing the features seen in the glass beads [8].

the vent on the ground. Depending on faster or slower cooling rates, the droplets of high-Ti mare basalt produced either quenched glass or crystallized beads. More information has been derived from other analyses. First, the iron redox state in these glasses and beads was equilibrated with an oxygen fugacity 1–2 log units below that of the Fe–FeO_x equilibrium [18]. Second, that the beads are coated with ZnS and other volatile materials indicate that they originated from gas-rich source regions.

These findings were quite unexpected because such pyroclastic (*pueros*, fire, *klastos*, broken) material point to past explosive volcanic activity, which is in principle caused by exsolution of volatiles (mainly water) out of the magma (Chapter 7.2). In other words, these glasses point to the former presence of rather large amounts of

water in the Moon. Recent discoveries of trace amounts of water in these lunar volcanic glasses [19] have also led to reject the traditional view that the Moon was virtually free of water. Since these contents are similar to those found in magmas produced at mid-ocean ridges on Earth (≈ 200 –700 ppm H₂O), they imply that lunar magmas originated from a region bearing about the same amount of water as the current Earth's upper mantle. Like on Earth (Chapter 7.2), the magma had deep sources, rose to the surface, thanks to a density lower than those of the surrounding rocks, and, through volatile release and expansion, fragmented and followed ballistic trajectories upon high-velocity eruption at the vent.

This new view has important implications regarding the formation of the Moon and on the way in which

volatile elements could have been retained upon a highly energetic giant impact. As the mantles of the Moon and Earth have similar compositions, however, it remains to explain why lunar samples are more depleted in volatile elements than terrestrial mantle rocks if the Moon formed from an Earth-orbiting disk of vapor and melt produced by a giant impact. Explaining the Moon's volatile depletion has been a long-standing mystery, yet it is a key piece of evidence about how the Earth–Moon system formed. In terms of a combination of dynamical, thermal, and chemical models, volatile depletion in the Moon can in fact be explained as preferential accretion of volatile-rich melt in the inner part of the disk where the Earth formed, rather than in the growing Moon, through volatile condensation upon cooling of the initially hot melt

[20]. Such a scenario illustrates how the Moon and Earth could have acquired important composition differences even though they resulted from the same giant impact.

3.2 Impact-Produced Glasses

A quite distinct kind of amorphous phase is also found in the regolith in the form of interstitial, flow-banded glass bonding together the constituents of the so-called *agglutinates*, namely small mineral grains, glass particles, or remnants of former agglutinates [21]. Along with a size of a few tens of micrometers to a few millimeters (Figure 5), agglutinates have a heterogeneous composition resulting from the presence of individual regolith

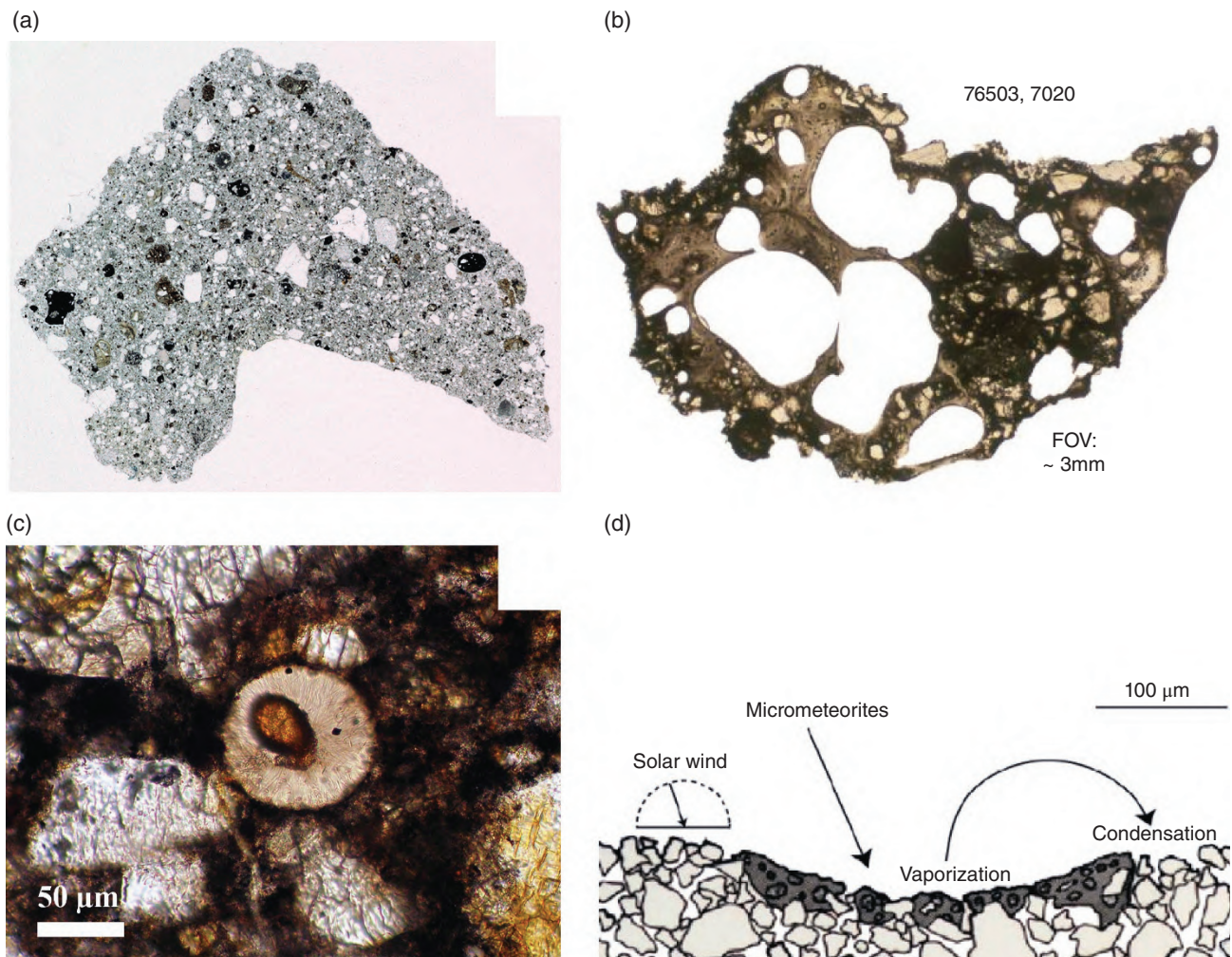


Figure 5 (a) Petrographic thin section of Apollo 16 regolith breccia 60016 where a few glass spherules are evident (http://meteorites.wustl.edu/lunar/60016ms_l.jpg). (b) Photomicrograph of a thin section of a large agglutinate fragment from the Apollo 17 regolith (Source: Photo courtesy Brad Jolliff). (c) Lunar impact spherules showing a variety of shapes, colors, and sizes hosted in the breccia of the lunar regolith brought to Earth by the NWA 8010 meteorite (<http://rse.s.anu.edu.au/research/annrep/ar2008/prise/hui.jpg>); observations similar to those made on Apollo 16 samples. (d) Sketch of the lunar surface as exposed to solar wind and constantly pounded by micrometeorites. Agglutinates and impact glass spherules can be found within the lunar soil and in microbreccias. Source: Credit: Larry Taylor.

particles. Other original features are highly irregular shapes and the presence of trapped bubbles and nanometric metallic iron globules. Given their rather uniform distribution in the regolith, the source of heat producing the cementing glass has to be extremely extended. This source is in fact the heat produced when, depending on incident velocities of up to tens of km/s, micrometeorites impact the fine-grained regolith, which then warms enough to melt and form the glass cementing mineral and rock fragments whose relative motion can then give rise to flow features. Upon melting, the material can in addition release the solar-wind-implanted hydrogen and helium, causing the presence of gas bubbles in the glass. As for the nanometric metallic iron inclusions, their size of a few tens of nm and their very low Ni content indicate that they formed through melting or vapor deposition of other lunar material rather than being brought to the Moon by meteorites.

Micron- to centimeter-sized glass spherules may form as well when a real meteorite impacts the lunar regolith. During the event, the melt splashes are thrown away and solidify by radiative cooling before landing. Their peculiarity in this respect is that the lack of an atmosphere and a gravity six times smaller than on Earth result in flight distances ranging from several meters to hundreds of kilometers. As a matter of fact, a single gram of lunar soil can give rise to more than 100 of these glass spherules. In general, their composition, size, and the shape allow them to be readily distinguished from pyroclastic spherules (Figure 5).

4 Cosmic Spherules

On Earth, small glass spherules have also been found, but in the unlikely environments of deep-sea sediments, polar ice sheets and, more recently, polar snow (Figure 6), very far from any volcanic source. Along with these completely melted spherules are also found partially melted, bubble-bearing, or scoriaceous material as well as unmelted, fine-grained, crystalline micrometeorites (Figure 7). All these samples thus were originally micrometeorites, in general related to the most primitive classes of carbonaceous chondrites, which were more or less heated upon descent in the Earth's atmosphere. These micrometeorites dominate the amount of extraterrestrial material accreted by Earth with an estimated flux of $40\,000 \pm 20\,000$ ton per year [23]. With a maximum grain size of about $200\,\mu\text{m}$, the glassy spherules account for around half of this amount.

Everything else been equal, heating and consequently changes to textures and mineralogical and chemical compositions are less intense for smaller particles and lower

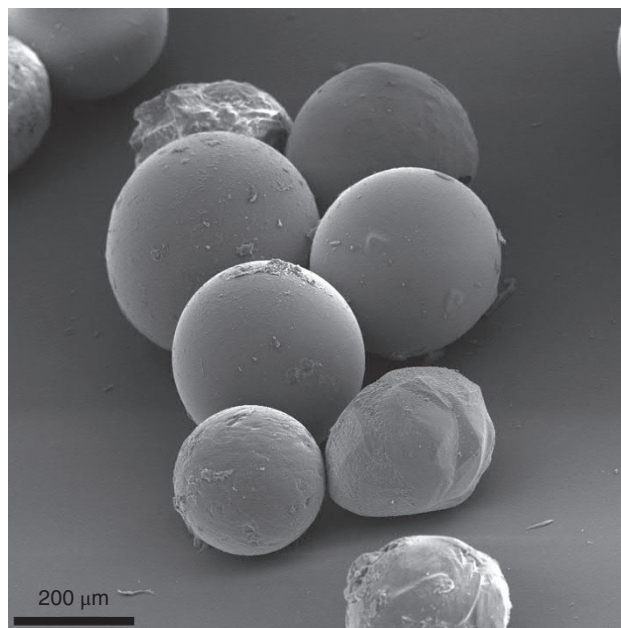


Figure 6 Stony cosmic spherules; largest about $300\,\mu\text{m}$ in diameter. Scanning electron microscope micrograph. *Source:* Credit: Graciela Matrajt, Cosmic dust web page.

entry angles and velocities in the atmosphere. But the initial velocity is not very high. When traveling in space, such small particles of matter absorb solar radiation and re-emit energy in such a way that their orbital momentum is slightly modified. As a result of this Poynting–Robertson effect, they travel in a spiral way toward the sun at speeds of only a few tens of km/s (Figure 8). If their pathway at altitudes of 80–120 km crosses the upper atmosphere, they are thus slowly decelerated to their free-fall velocity. This is why these interplanetary dust particles or micrometeorites have been collected not only in the stratosphere by NASA aircrafts, but also on the ground. And the reason why they represent an important source of unbiased information about the nature of asteroids and comets [24] is that, in contrast, the much rarer and bigger meteorites reach the ground only if they are carried away by adequate gravitational instabilities and if they are large and strong enough to survive atmospheric entry without fragmentation or destruction.

To take full cosmochemical advantage of these samples, however, it is useful to determine the conditions under which the texture and mineralogy of the micrometeorites were modified. Of course, the spherical shape of the glass spherules result from surface tension effects on a material completely melted above $1400\,^{\circ}\text{C}$, which is then quenched before reaching the ground. More interesting, the manner in which the textural and chemical diversity of spherules depend on oxygen fugacity – i.e. on the

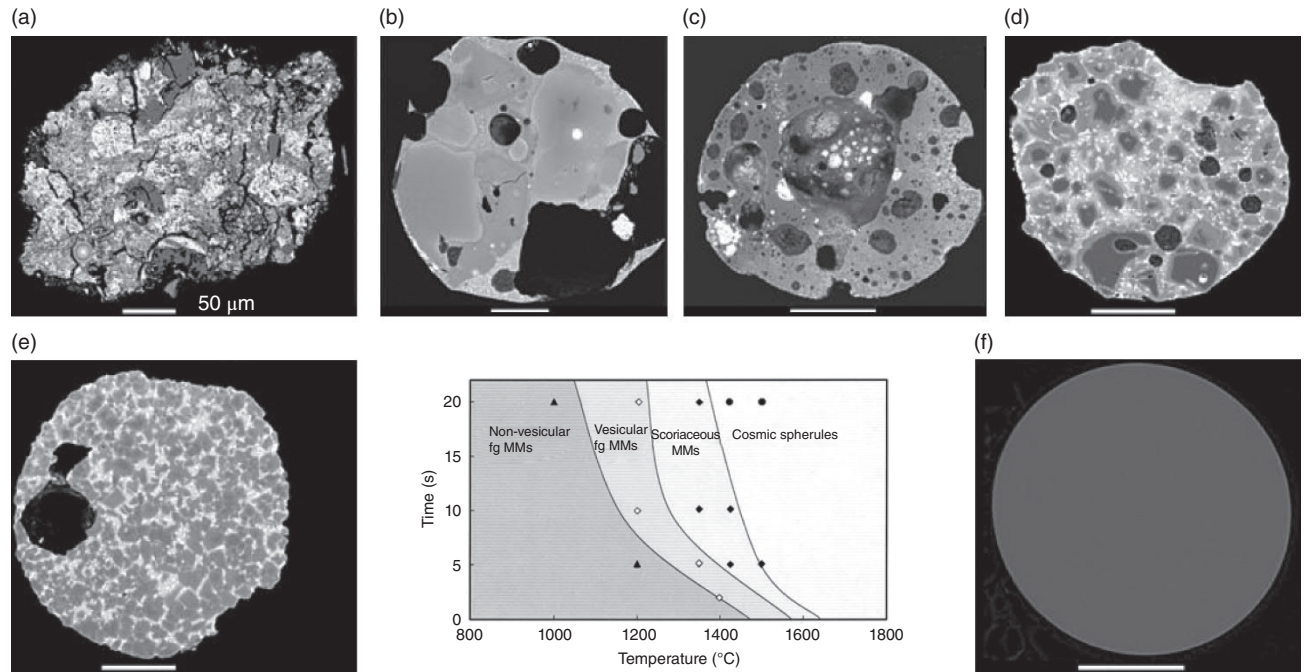
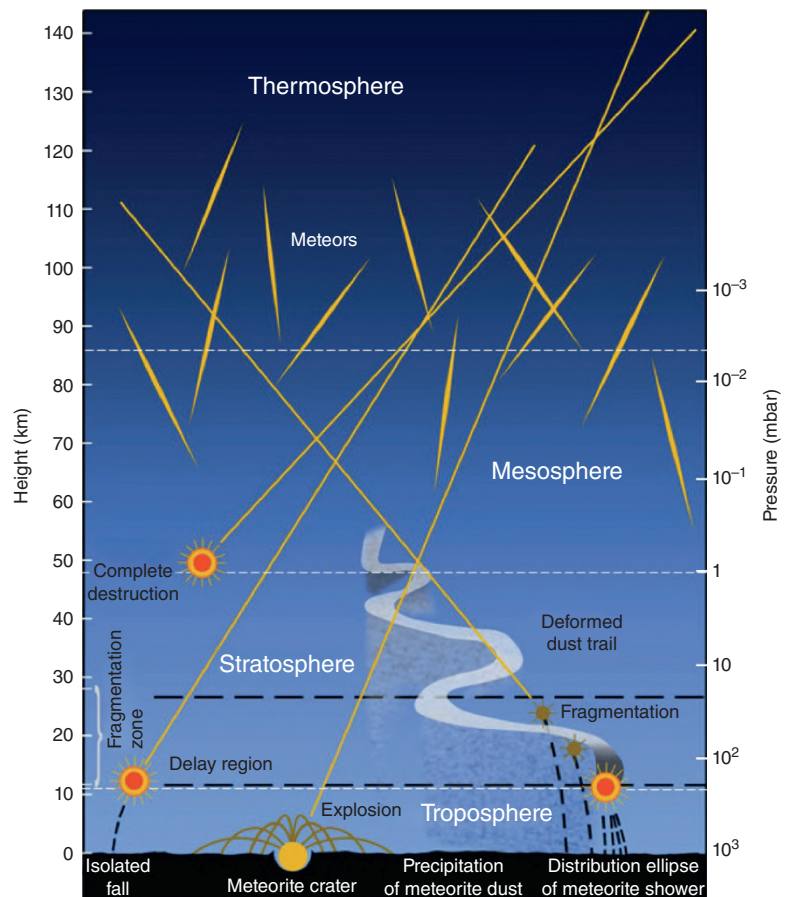


Figure 7 Influence of the initial speed and angle of entry in the atmosphere on the degree of heating, and thus on the texture of micrometeorites. (a) Fine-grained unmelted. (b) Coarse-grained unmelted. (c) Scoriaceous. (d) Relict-grain bearing. (e) Porphyritic. (f) Fully melted glass spherule. Also included are the conditions of heating suffered by large micrometeorites (200–400 μm) during atmospheric entry deduced from their texture and mineralogy [22].

Figure 8 Meteoroids entry in the Earth's atmosphere. Most tiny particles burn up more than 70 km above the surface, producing ionized gas trails called meteors. Larger objects can reach altitudes of 10–30 km before fragmenting, giving rise to a meteorite shower on the ground when fragments survive the burst. Largest objects not significantly decelerated, hitting the surface and producing a hypervelocity impact crater. *Source:* Colorized and slightly modified version of a classic educational illustration by E. L. Krinov; Image Credit: LPI.



altitude in the atmosphere where they break down – the duration of the heating pulse, and evaporative loss upon entry have been determined experimentally (Figure 7 and Table 1). Specifically, peak temperatures and cooling rates increase from porphyritic, to barred-olivine, crypto-crystalline, and glass spherules, and then to Ca–Al–Ti-rich (CAT) spherules.

This heating sequence leads to increasing CaO, Al_2O_3 , TiO_2 , and MgO and decreasing FeO contents. These trends are consistent with the results of mathematical modeling and experimental simulations of heating and evaporation performed with chondritic and solar chemical compositions [25]. Despite rather severe entry conditions, most of the cosmic spherules thus broadly preserved the original chondritic compositions and provide a means of sampling meteoroid types not represented by presently collected meteorites.

Numerical simulations of the atmospheric flight of micrometeoroids have also been performed for ranges of initial diameters (10–1000 μm), initial entry velocities (11–72 km/s), and entry angles (0–90°) [23]. It appears that peak temperatures experienced by submillimeter micrometeoroids rarely exceed 1700 °C. The maximum temperature and mass loss rate generally occur at altitudes between 85 and 90 km within about 1 second of the heating peak (Figure 8). A melted particle typically was calculated to spend about 2 seconds above the liquidus. In spite of this short time, the mass loss was important since typical cosmic spherules were 1.5–2 times bigger before melting, about half of all survivors larger than 70 μm being melted. This result does not match well the observation that many unmelted particles of up to 200 μm in size have been recovered in the polar collections.

Other simulations of the atmospheric entry of micrometeorites have thus been made, but none of them has yet yielded more accurate results because of the great many parameters involved, among others the nature, speed, and size of the precursor, friction effects, or the pressure, temperature, or chemical composition of the atmosphere.

During the deceleration of the extraterrestrial material through the Earth's atmosphere, one of the most ubiquitous changes is the precipitation of tiny spinels resulting from partial melting and subsequent crystallization of the meteoritic material. These *cosmic spinels* differ from their terrestrial counterparts by their higher Mg, Ni, and Fe^{3+} contents and larger variations in composition. These cosmic spinels rapidly precipitate from partial melts produced upon meteoroid entry in the Earth's atmosphere. Because the atmosphere becomes progressively more oxidizing as the meteoroid penetrates deeper in the atmosphere, the spinel compositional range may represent a record of the ballistic trajectory of the object during its

fall to the ground and, thus, might shed some light on its provenance.

To understand better the factors controlling the spinel chemistry, pulse-heating experiments simulating atmospheric entry of extraterrestrial objects have been carried out on small samples of the well-known Orgueil carbonaceous chondrite as proxies of incoming micrometeoritic material [26]. Owing to the rapid crystallization kinetics of cosmic spinel, the Al_2O_3 content and FeO/ Fe_2O_3 ratio of the mineral have indeed been found useful to determine the entry conditions of meteoritic material in the Earth's atmosphere. As an example, spinels with high Al_2O_3 content and FeO/ Fe_2O_3 point to a very rapid deceleration and a relatively high incident velocity of cosmic spherules (Figure 8).

5 Terrestrial Versus Extraterrestrial

The classical model for the formation of the Solar System invokes the gravitational collapse of a cold molecular cloud of interstellar gas, its heating, and the formation of a central star. A flattened spinning protoplanetary disk of dust and gas surrounding the protosun extends for 100 AU or so. Initially hot, this disk later cools (T-Tauri stage). Since the heat flux is greatest close to the sun and at places where the cloud is the densest, the disk is hotter near the center and cooler farther away, suggesting a temperature decrease with increasing heliocentric distance from the protosun in the early solar nebula. On average, it is assumed that temperature drops rapidly from a few thousand degrees within 1 AU to a few hundred farther out. As the protoplanetary disk cooled down, the gas temperatures dropped below the condensation temperatures of refractory materials, like aluminates, silicates, metals, which formed in the inner Solar System at less than 1 AU. Water ice (snow line) followed suit at around 3–4 AU before other volatiles (ammonia, methane, carbon dioxide, nitrogen) farther out. Clumping of these rock/metal condensed materials into planetesimals in the inner Solar System and chunks of ice in the outer Solar System would eventually yield the actual structure of the Solar System with, in particular, its division between inner terrestrial planets and outer gas giant planets [27].

What could now be said about the differences between terrestrial and extraterrestrial materials? On Earth, basalts show a considerable variety although their chemical signatures have been inherited from terrestrial mantle rocks melted under a limited range of pressure–temperature conditions. In contrast, the chemical and isotopic compositions of meteorites indicate at least many tens of distinct parent bodies. More specifically, the diversity of achondritic (i.e. basaltic or igneous)

meteorites suggests that a significant population of such asteroid-sized bodies underwent internal melting and differentiation during the first several million years of the Solar System [28]. In this scenario, early accreting planetesimals retained sufficient short-lived radiogenic isotopes to melt partially or fully the interior except for a conductively cooled crust whose thickness was between a few and several tens of km. Material near the surface of this crust would have undergone minimal metamorphic heating and become the source region for nonmetamorphosed chondritic meteorites. Deeper material from the crust would have experienced increasing degrees of metamorphism and eventually underwent partial melting and differentiation. In this model [29], the preservation of either a chondritic or an achondritic crust on a differentiated body would thus depend on the positive or negative buoyancy of silicate melts produced at depth with respect to the overlying crust (Figure 9).

Asteroids are small, lack atmospheres, and were heated quickly by short-lived radioisotopes (^{26}Al , ^{60}Fe , etc.) instead of the much longer-lived isotopes of K, Th, and U that have mainly powered the heating of planet-embryos and planets. Relative to the Earth, their volcanic activity thus had to be very different. There are indeed large differences in the depth range over which melts form, the amount of melting that takes place in any given time interval, the rates at which melts migrate, the amounts and compositions of their volatiles, and the way in which they erupt when reaching the surface when they do so [30]. In the absence of plate tectonics, intense bombardments leading to the melting of surface materials

at scales varying from those of spherule to magma ocean make melt and glass production (and their record or signature in meteorites) even more complicated than might have been expected. Although asteroid surfaces are subjected to weathering in space by cosmic rays, solar wind implantation, or micrometeorite bombardments, their airless environment and extremely low H_2O partial pressures account for the astonishingly good preservation of their glasses despite their extremely old ages.

Finally, it is worth noticing that the recent discovery of terrestrial (rocky) exoplanets has pushed the limit of “extraterrestrial glass factories” even further away in our galaxy, since many small planets orbiting very close to their star experience intense irradiation and tidal forces so that their surfaces are mostly covered by magma [31]. Hence, they constitute a new class of celestial objects called *lava ocean planets*.

6 Perspectives

With respect to glass science, the most striking conclusion drawn from the study of extraterrestrial matter is that glass may actually be kept in its metastable state for billion years in the 170–400 K temperature interval of the lunar surface as long as water and other weathering agents are lacking. The commonly held idea that glasses would necessarily crystallize after not too long periods of time thus is clearly invalidated. On the other hand, the chondrules of primitive meteorites have experienced aqueous alteration of their metal and glass phases within

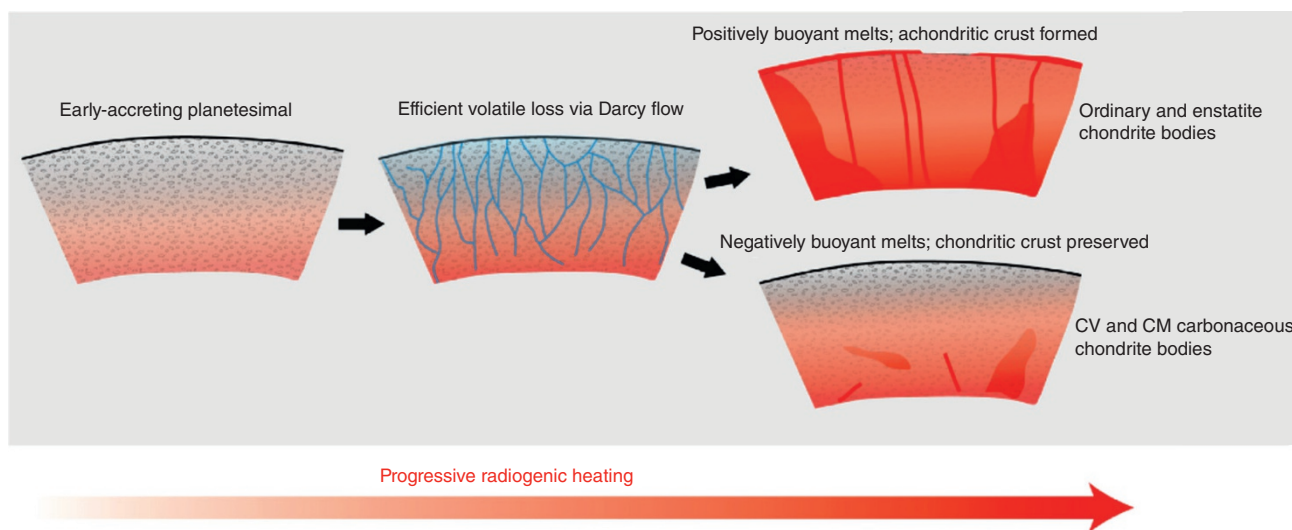


Figure 9 Sketch of silicate melt ascent in planetesimals. Moderate radiogenic heating leads to formation of free volatile phases. Most volatiles are efficiently removed via Darcy flow, resulting in volatile-poor silicate melts, whose buoyancy depends on bulk composition. Melts of CV and CM carbonaceous chondrites are negatively buoyant, leading to preservation of an achondritic crust. On the other hand, enstatite chondrite melts are likely to breach the surface; ordinary chondrites are an intermediate case [29].

their parent bodies. They might thus represent valuable model systems in studies of alteration and corrosion processes at the glass–metal–clay interfaces relevant to the long-term evolution of nuclear waste-glass packages under geological repository conditions [32]. The same would apply for predictions of elemental mobility upon alteration in anoxic environments, which are relatively rare on Earth.

From a cosmochemical standpoint, extraterrestrial glasses will bring more key information on the evolution and activity of the Solar System, thanks to their varied compositions and conditions of formation and their exceptionally long-term durability. Glass (melt) compositions will, for instance, be used as thermochemical and isotopic sensors of the gaseous environment within which these materials formed. In particular, glass compositions should exert strong constraints on the nebular gas composition itself (i.e. partial pressures, isotopic signatures) in the regions of the protoplanetary disk where chondrules formed.

The most important transformation undergone by a magma is its solidification upon cooling. The process is complex, however, if the heat released upon crystallization causes partial remelting of the material. Hence, ascertaining the processes that eventually gave rise to a sample made up of crystals, glass, or a mixture of glass and crystals can be difficult. Determinations of time–temperature–transformation diagrams for selected extraterrestrial glasses (chondrules, green glass, etc.) will thus be an important task to determine the cooling/heating rates and thermal histories experienced by chondrules and, then, to characterize their peculiar environments of formation in the solar protoplanetary disk.

Regardless of the details of the processes, an important feature is that much energy has been available during the lifetime of the Solar System through large-scale gravitational instability in the disk, accretion, short- and long-lived radionuclides, and collisions for transforming dust clouds into km-sized planetesimals, then into 1000 km-sized planet embryos and, eventually, the real planets. From its tumultuous birth to the relatively quiescent present day, the Solar System has therefore hosted a plethora of environments in which conditions have been suitable for producing partially molten materials, liquids, and magmas, and depending on their cooling history, pyroclastic flows, basaltic lavas, or plutonic rocks [3].

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7.2

Geological Glasses

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1 Introduction

In the solar system natural processes have been producing glasses ever since its beginnings 4.5 billion years ago (Chapter 7.1). On Earth, in particular, they have done it since time immemorial with the well-known processes of casting, blowing, and even drawing. As a striking example, nature has been producing SiO_2 glass in several ways, whereas this material was first produced artificially only in 1813 [1]. Unknowingly, man has thus been imitating nature, but at a scale that, even today, remains modest. Whereas the annual world production of glass is about 100 million tons, it represents only about 1/1000th of the total amount of magma reaching the Earth's surface every year. Even though only a fraction of the magma vitrifies, it does represent a very large volume of naturally produced glasses.

Nature also pioneered low-temperature processes that remain to be duplicated artificially. A case in point is the extremely pure amorphous silica synthesized by the unicellular diatom algae for their tests or by a great many sponge species for their spicules. Because these materials are dealt with in Chapter 8.1, here we will restrict ourselves to purely inorganic glasses. Their compositions, textures, and geological occurrences point to widely different heat sources. By far the most common and abundant glasses originate from the Earth's interior so that they provide unique insights into a variety of magmatic and volcanic processes. Other natural glasses derive from heat sources from the atmosphere or space. As such, these glasses give valuable clues about phenomena that now seldom occur at the Earth's surface but could have been much more frequent in a distant past.

Because geology is first and foremost a historical discipline whose goal is to reconstruct the evolution of the Earth since its formation, the main purpose of this chapter will be to briefly depict information that can be drawn on Earth's significant events from the study of natural glasses. As a preamble, the compositional diversity of natural glasses will be reviewed. Attention will then be paid to two forms of almost pure silica glass, *fulgurites* and *Libyan Desert glass*, melted by lightning and approaching extraterrestrial bodies, respectively. Their source is mostly quartz. Resulting from the impact of large meteorites, *tektites* with their more varied compositions will also be dealt with. Next, we will consider the predominant magma-related glasses. As a matter of fact, all volcanic rocks contain some glass with a proportion that increases with the viscosity of the melt. This proportion is thus relatively low in the SiO_2 -poor basalts but can reach >90% in the SiO_2 -rich obsidians, which gave these glasses a very great practical importance before the invention of glassmaking (Chapter 10.1). Because natural glasses interact with their environment, we will also summarize the early physical and chemical transformations they may undergo, once they have formed, referring to Chapter 7.3 for a detailed description of the corrosion reactions that eventually convert them into completely new phases.

2 Compositional Diversity of Natural Glasses

The composition of geological glasses is generally complex. There are about 10 *major* elements with contents higher than 0.1 wt % as expressed in terms of oxides (Table 1). Virtually the whole periodic table is also present, but most of the other elements are usually not considered because of their vanishingly

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Table 1 Composition of some natural glasses and average compositions of some volcanic rocks.

Wt %	Basalt ₁	Basalt ₂	Basalt ₃	Phonolite	Obsidian	Rhyolite	Libyan glass	Fulgurite	Rochechouart	Tektite
SiO ₂	48.4	51.9	48.8	56.2	73.7	72.2	96.6–99.3	97.6	65.1	70.4–77.2
TiO ₂	1.5	1.5	1.1	0.6	0.2	0.4	0.1–0.2	0	0.6	0.7–0.8
Al ₂ O ₃	16.9	14.8	15.9	19.0	13.8	13.2	0.5–2.6	1.5	14.8	10.8–13.4
FeO _t	9.3	8.8	9.0	4.6	2.1	2.9	0.1–0.4	0.2	9.9	4.0–6.7
MnO	0.2	0.1	0.2		0.1	0.1				
MgO	8.5	7.8	9.7	1.1	0.1	0.5	0.0–0.5	0	1.2	1.6–4.2
CaO	11.4	11.7	11.2	2.7	0.8	1.5	0.0–0.02	0.4	0.2	1.5–3.9
Na ₂ O	3.1	3.0	2.4	7.8	4.9	4.0	0.0–0.01	0.3	0.2	1.2–1.6
K ₂ O	0.1	0.1	0.1	5.2	4.2	3.8	0.0–0.01	0	10.9	1.9–2.4
P ₂ O ₅	0.2	0.2	0.1				0.0–0.01			

Basalt₁ and basalt₂ are MORB glasses. La/Sm ratios range from 0.67 to 0.75 [2]; basalt₃ MORB [3]; phonolite, rhyolite, fulgurite, Rochechouart (P. Richet, pers. comm.); obsidian [4]; Libyan glass: K/U from 41 to 219, Zr/Hf from 37 to 60, Zr/U from 137 to 304, La/Sc from 6 to 13, Ir from 0 to 0.2 ppm, Cr from 1.8 to 10.4 ppm [5]; Sr⁸⁷/Sr⁸⁶ isotopic ratios for tektites: 0.718–0.724; Obs.: total may differ from 100% due to missing components (mainly water), iron oxidation state and normalization; FeO_t is the total iron content as Fe²⁺.

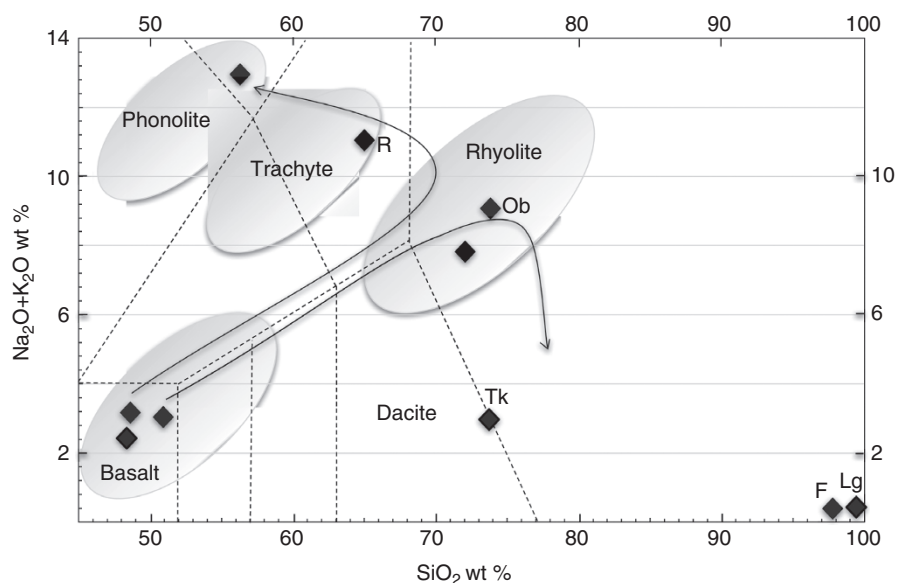


Figure 1 Compositions of natural glasses in the simplified total alkalis vs. silica diagram: ranges of volcanic rocks (grayish fields) and most common evolutionary trends (arrows). Some particular compositions indicated for convenience: R, Rochechouart; Ob, obsidian; Tk, tektite; Lg, Libyan glass; F, fulgurite.

low concentrations. Exception is made for a variety of *trace* elements whose contents can be only a few to around 1000 ppm, however, because their concentrations vary much more than those of major elements as a result of a greater sensitivity to the processes that come into play between original melt formation and eventual vitrification. In this way they represent fingerprints of geological glasses having similar major element contents, which are, for instance, extensively used in archaeometric studies of obsidians to identify their sources and to investigate trade in Prehistory (Chapter 10.1).

On close inspection, however, it appears that the concentrations of major elements do not vary randomly from one glass to another. Broadly speaking, increases in SiO₂ contents are related to decreases in alkaline earths and increases in alkalis. These variations are strongly correlated as illustrated by plots of SiO₂ contents against Na₂O + K₂O for the most common volcanic rocks and glasses (Figure 1). From the primary SiO₂-poor to the most evolved SiO₂-rich compositions, the impressive diversity of magmatic products can thus be reasonably well described with just a few parameters. There are nonetheless clear

exceptions to those trends characterized by extremely high SiO_2 contents. They will be described first in view of this chemical simplicity.

3 Fulgurites: The Petrified Lightnings

Fulgurites are famous in Sahara. Their compositions are there very close to that of pure silica (Table 1). They are found on sand dunes, generally in the form of fragile hollow pieces 5–20 mm in diameter and typically ~10 cm long (Figure 2a), and which are in fact fragments of tubes whose original length can reach a few meters. Occasionally, they are also found as small beads. Their widespread occurrence in sandy deserts points to rather common melting events. Lightning (*fulgur*, in Latin) is their obvious source, causing such high temperature rises ($>1600^\circ\text{C}$) that quartz grains may melt or even vaporize to create hollow, channel-like structures. The morphology of the fulgurite tubes then indicates the lightning pathway along which quartz melted on the ground.

Actually, a typical lightning involves a current of 30 kA and an energy of 500 MJ. Since the enthalpy of fusion of quartz is 9.4 kJ/mol [6], a single strike could cause the melting of 3000 tons of this material. Even when taking into account branching of the lightning on its way to the surface, one concludes that only an extremely small fraction of the energy is expended to melt and vaporize sand. Clearly, the rate of heat transfer is the limiting factor of the process since the lightning energy is released in a fraction of a millisecond at most. The small diameter of the glass tubes, within which the melt was vaporized and on which sand grains are glued, is thus distinctive features of fulgurites resulting from this brevity. This amorphous silica, named *lechatelierite* (after Henry Le Chatelier [1850–1936] known in particular for his moderation principle in thermodynamics), exhibits typical flow structures and vesicles.

To be most efficient, the transformation would require powdered starting materials. In nature, however, silicate sand is found mostly in the form of quartz, one of the most stable minerals at the Earth's surface. Thanks to its lack of cleavage, high hardness, and low solubility in aqueous solutions, it may accumulate under the action of wind or water but has too high a melting point and is too viscous when melted to yield a bulk glassy phase. A lightning strike can in contrast melt any silicate rock partially or even totally when the liquidus temperature is much lower than that of quartz, especially if the rock is fragmented as found in explosive volcanism (Figure 2b). One then obtains a *rock fulgurite*, but the small amounts of glass produced in this way often quickly disappear through alteration, which makes them difficult to observe.

4 Impact-Related Glasses

4.1 Impactites

As indicated by its name, Libyan Desert glass (Figure 3) originates from a restricted area of Sahara where it formed 28.5 million years ago. It is found on quartz sand dunes as clear, pale, yellowish scattered fragments with a size of up to a few hundred grams. The Egyptians valued this rare and beautiful material and used it, for instance, on the pectoral chain of Tutankhamon (Cairo Museum, Egypt) to make the yellow-green scarab at the heart of his pendant [7].

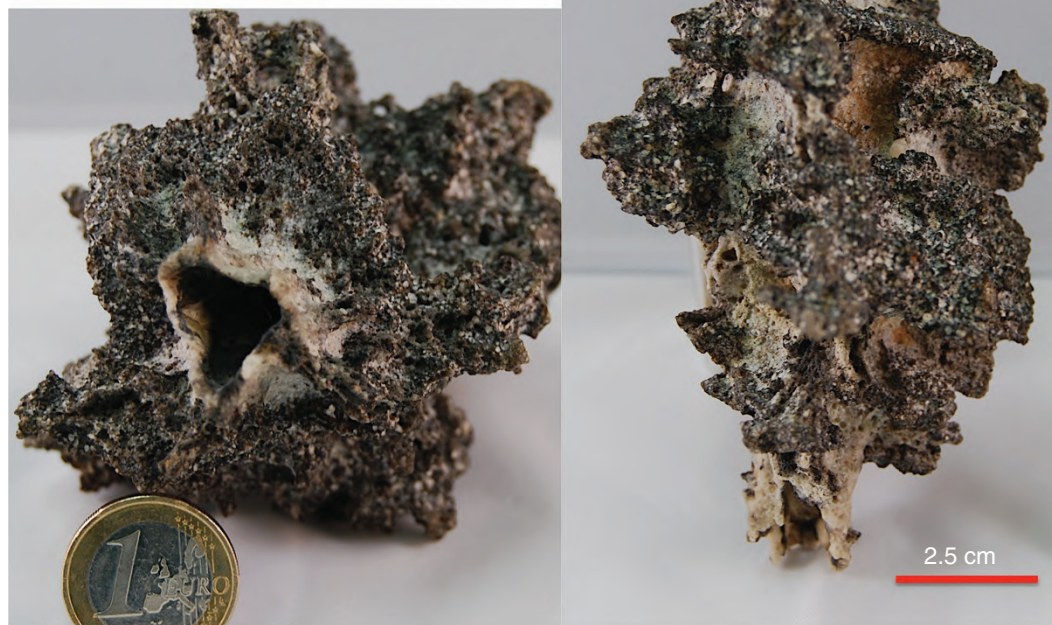
This clear, shiny glass carries few inclusions (Figure 3) and also has a unusually simple composition with a SiO_2 content ranging from 97 to 99.3 wt % (Table 1), which makes it not only translucent but also transparent. In addition, the bigger size of the samples, when compared with fulgurites, and their wide scatter indicate that the melting event was of a much longer duration and larger spatial extent, whereas the well-polished surface of the glass caused by sand blasting points to a not so recent event. As for the lack of any sharp crater observed in the region, it should exclude the impact of an extraterrestrial body as the heat source.

Two other explanations have been proposed, involving the disintegration of either a comet or a meteorite at an altitude above the ground low enough to cause rather large amounts of sand to be melted by the heat released in the atmosphere by a shock wave, but high enough to blast this melt and disseminate it over a few thousands of km^2 .

Clues on the origin of the Libyan Desert glass have been provided by a small carbon-rich stone found in the same region, in which patches of sub- μm diamond represent spectacular evidence for the attainment of very high pressures. Along with the results of isotope analyses, this feature has been interpreted as indicating that Libyan Desert glass formed upon the burst caused by the explosion of part of a cometary nucleus after its entry in the atmosphere had caused the loss of volatile hydrocarbons and ice and the intake of heavy noble gases (Ar, Kr and Xe) [8]. The rare-earth element contents of Libyan glass, i.e. La/Y ratios from 6.5 to 10.9 [5], do point to desert sand as the source material, but magnesium enrichments of up to 0.5 wt % (Table 1) require an admixture of chondrite meteorite material (Chapter 7.1) to be explained. Some additional rare trace elements such as Co, Ni, and Ir have also been found in desert glass in similar proportions as in chondrites [5].

The uniqueness of Libyan Desert glass thus does not seem to result so much from the negligible fraction of the Earth's surface covered by sandy deserts, but mainly from the fact that disintegration of a comet

(a)



(b)



Figure 2 Fulgurites. (a) Silica fulgurite as seen along the horizontal axis and vertically: irregular cavity consisting of milky glass ceramic material still surrounded by different layers of partially molten individual sand grains. Black color due to iron oxide impurities. (b) Rock fulgurite on the slope of the Teide basaltic volcano (size of about 10 cm; Tenerife, Canary Islands). *Source:* Photo J. Roux.

or meteorite well above the ground should be very rare. The well-known occurrence of the Tunguska event [9] on 30 June 1908 when 2000 km² of forest were wiped out in Siberia without leaving any

observable trace of extraterrestrial matter supports such an interpretation. In this case, however, agreement has not been reached yet on the nature of the incoming body.



Figure 3 Libyan Desert glass, with polished surface produced by sand blasting under strong winds. The small inclusions are impurities from the melted sand or tiny fragments from the impacted cosmic material.

4.2 Tektites

As discovered only in the twentieth century, glasses named *tektites* (from the Greek *tēktos*, molten) may be also produced by large meteorites impacting the Earth. They are usually very dark in color (black, brown, greenish) with a size ranging from a few to several centimeters. Lighter colored and transparent tektites such as *Moldavites* are exceptionally rare. These may be emerald green with bubbly inclusions. Although related to Libyan Desert glasses, tektites differ markedly from them in their chemical and isotope compositions that closely resemble instead those of upper continental crustal rocks (Table 1).

They are found on the ground or at some depth. From their compositions, they have been grouped in four distinct *strewn fields* in North America, Central Europe, Western Africa and Australia/Asia. Whereas the third one is more or less restricted to Ivory Coast, the last is really large since it extends from Tibet to Australia, covering approximately one third of the Earth's surface. By far, tektites from this Australasian strewn field thus are the most common.

Because of their very low water contents and very reduced iron states, implying melting temperatures higher than 1700 °C, tektites are considered to be molten terrestrial ejecta, which have been originated by the hypervelocity impact of a cosmic body (meteorite) hitting the Earth's surface [5]. The splashed form and shallow bowl aerodynamic shapes of tektites are due to ablation of molten material in the atmosphere and in addition evidence their ejection into the stratosphere (Figure 4).

4.3 Other Impact Glasses: The Example of Rochechouart Pseudotachylites

Even though the presence of typical lavas in the Rochechouart area in central France was observed as early as the late eighteenth century, no trace of a volcano was ever



Figure 4 Tektite from the Australasian strewn field. Aerodynamic shape resulting from ablation of molten material upon reentry in the atmosphere after ejection into the stratosphere.

found there. For good reasons, since it was established in 1969 that melting was actually produced by a meteorite impact 200 million years ago when F. Kraut discovered the first shocked quartz under the microscope in local rock samples.

Along with previous field observations on a variety of impact structures around the world (e.g. the Nördlinger Ries, in Germany, the Meteor and Sudbury Craters, in the USA, the Chicxulub crater in Yucatan), experimental laboratory work on friction melting has shed new light on the origin of structures such as Rochechouart. In particular, it has been demonstrated that shock waves may cause rock fragmentation (*brecciation*) and local temperature rises eventually leading to melting. Impacted rocks may be recognized by macroscopic and microscopic features. Planar deformation in rock-forming minerals and the presence of high-pressure mineral polymorphs (e.g. coesite and stishovite from quartz or diamond from graphite) are strong evidence of high-pressure and shock waves in the so-called *diaplectic* glasses. These changes result from pressure-induced amorphization at low temperature (Chapter 3.10) and of “normal” glasses formed through actual melting [5].

Recent detailed studies in melt and clasts from a vein system containing melt rock and hydrothermal crystallization from the Champagnac quarry (Rochechouart structure), however, revealed new aspects regarding the shock phenomena [10]. There the melt fraction was actually produced by friction during lateral shear movements after the impact. Circulation of hydrothermal fluids (up to 700 °C, high P_{H_2O}) then caused the plagioclase feldspars of the breccia clasts and immediate host rocks to transform into mica. Long-term tectonic activity (crosscutting fractures) and additional hydrothermal

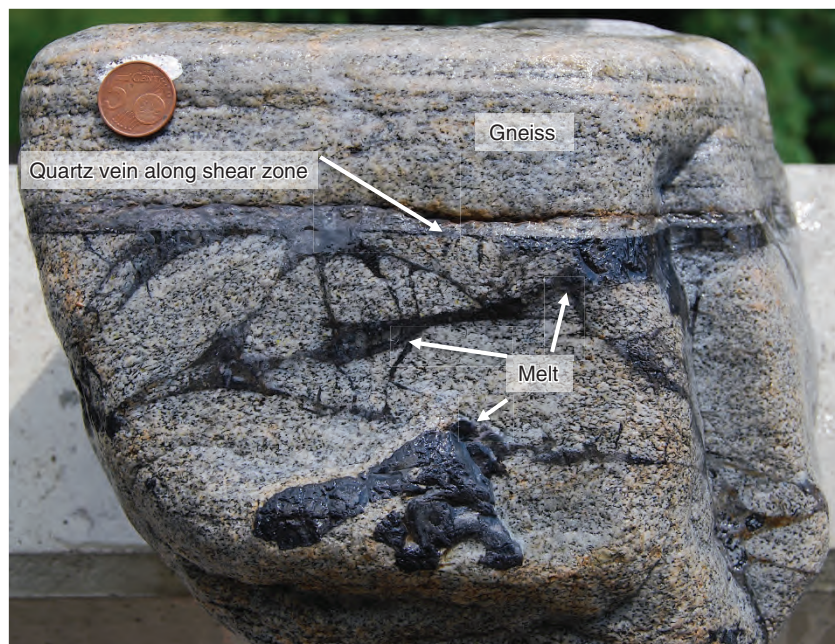


Figure 5 Pseudotachylite as formed by melting of a gneiss (consisting mainly of quartz and feldspar), along mostly linear planes of stress concentration. Frictional melt reintruding the source rock and suggesting a relatively high viscosity through the lateral variation in thickness and morphology (Silvretta, NW side of the Unterengadiner tectonic window, Swiss Alps, collection of the Museum Reich der Kristalle, Munich).

modifications took place, which induced later partial devitrification of the glassy matrix.

Since the compositions of these glasses depend on the source rocks, they may be highly variable even within the same impact structure (Figure 1; Table 1). They include in particular *pseudotachylite* (from the Greek *takhys*, swift), which are friction-melted glasses [11] whose name distinguishes them from *tachylites*, the basaltic glasses formed in conspicuous volcanic terrains. Pseudotachylite is black and consists of angular and rounded wall rock fragments enveloped by a microcrystalline to glassy matrix (Figure 5). When these rocks are affected by a high stress field and additional mechanical rebound, part of the deformation energy is transformed into so much heat that the material partially or completely melts and the resulting liquid is injected along fractures. The compositions of the glasses then simply reflect those of the total or partial melting from parent rocks.

When such glasses are found in nature, they reveal that a pre-existing natural material has been affected by a high stress field and additional mechanical rebound. So, pseudotachylites can also be formed in volcanic edifices [11] or, more generally, when melting is observed along a normal or inverse fault plane [12]. The presence of pseudotachylite thus provides quantitative information on the tectonic forces involved in the process. Frictional melting of natural rocks has been simulated in the laboratory through the frictional slip of two rock surfaces at high velocity rates (~ 1.3 m/s). The conclusion is that stresses of around 10 MPa and slip distances

lower than 15 cm are required to ensure rock melting [11].

5 The Basalt Factory

5.1 The Ubiquitous Basalts

The most common volcanic rocks on Earth are basalts. They typically have SiO_2 contents ranging from 48 to 52% (Table 1). Most basaltic magmas are erupted along 60 000 km of mid-oceanic ridges and hot spots, where they continuously produce not only new oceanic floor but also archipelagos and islands such as The Azores, Hawaii, Iceland, or La Réunion. They are in addition found in continents where erupted volumes of millions of km^3 have given rise in the past to the immense plateaus of Dekkan, in India, or Paraná-Etendeka, in Brazil/Africa. They are very fluid thanks to their relatively low contents of the network-forming elements Si and Al (Table 1), which allow them to ascend rapidly to the Earth's surface without cooling down too much along the way. With a viscosity of the order of 100 Pa·s, they are still very fluid at typical eruption temperatures of about 1200 °C so that they can flow rapidly down the slopes of the volcano where, depending on relief and erupted volume, they can travel up to a few tenths of km before coming to a rest. On the other hand, the viscosity of the melt increases when the lava cools down, but the main factor is crystallization. Magnetite (Fe_3O_4) generally precipitates first



Figure 6 Pelé's hair and tears (small black droplets) from the Piton de la Fournaise volcano. Source: Photo P. Richet.

and then serves as nucleating sites for other minerals such as pyroxenes. In the end crystals with a variety of shapes and size are observed within a residual glassy matrix [13].

5.2 Pelé's Hair and Reticulite

When an eruption of fluid magma gives rise to the high lava fountains that have been popularized by films and videos, with a little bit of luck one can find on the ground glass fibers from 1 to 500 μm thick known as Pele's hair (from the name of a Hawaiian goddess) (Figure 6). These were first described at the Piton de la Fournaise (La Réunion island) by Bory de Saint Vincent in 1804. Except for somewhat larger diameters, they are strikingly similar to industrially produced rock wool fibers (Chapter 9.3), showing also the presence of entrapped globules of non-drawn glass. They are simply drawn hydrodynamically at the eruption event where the lava jet can reach speeds over 35 m/s. Why are such high speeds achieved? The answer is that exsolution of gas (mainly water) upon decompression during magma ascent is the driving force of volcanic eruptions. The presence of bubbles not only increases the buoyancy of the melt and bubbles but also exerts such a hydrodynamic ascending force that the magma gets fragmented even before reaching the surface and being stretched as fibers. Even though Pelé's hair are common products of volcanic eruption, their intrinsic fragility and high surface/volume ratios make them sensitive to weathering so that they rapidly disappear.

Glass blowing is the other process at work with such fluid magmas. Taking place at all scales when gas bubbles grow upon decompression, it is actually revealed in many volcanic rocks by the presence of bubbles. In some cases,



Figure 7 Reticulite from unknown origin. Source: Photo P. Richet.

the volume fraction of bubbles is so large that the material can be considered as a frozen in foam called *reticulite* (Figure 7). When very large bubbles explode, very thin glass membranes can form. But they are even more fragile than Pele's hair.

5.3 Water-Quenched Glasses

Quenching is definitely faster and most efficient when a melt is poured in water. In lavas the proportion of glass thus is the highest for submarine or lacustrine eruptions. A typical *pillow-lava* morphology, resulting from the rapid vitrification of the surface of the advancing flow, can be observed. Over a thickness of a few mm to cm, an essentially *tachylite* phase is thus preserved. The pillow lava has a glassy crust including only very tiny crystals, below which the proportion of glass decreases to reach the typical 50% fraction of basalt. Given that about 75% of magma erupt as submarine basalt, these glasses are by far the most abundant that form at the Earth's surface. As a result of rapid quenching, however, the glass surface is under tension or highly stressed. It allows bacteria and other organisms such as sponges to take advantage of it, either to leach out cations or induce changes in the iron oxidation state, which could have been a potential energy source for early life [14]. As described in the following chapter, however, the glass from a pillow lava rapidly transforms to other phases upon reaction with either fresh or seawater. Finally, one can note that basalt glasses are also called *sideromelane* (from the Latin *sider*, star, and Greek *melanos*, black).

5.4 Columnar Jointing: The Role of the Glass Transition

In an aerial environment a striking feature of volcanic rocks is *columnar jointing*, whereby a thick enough lava flow fractures upon cooling to form rather regular polyhedral prisms, generally pentagonal or hexagonal, perpendicular to the upper (the air) and lower (the ground) cooling surfaces. That they are most often observed for basalts is simply because of the more frequent occurrence of these lavas, but an interesting fact is that the section of the prisms tends to increase with the SiO_2 content of the lava. The similarity of the shape of the columns to those of crystals forming in aqueous solutions leads early eighteenth-century geologist to assume that volcanic rocks precipitated from a primordial ocean. When N. Desmarest demonstrated in 1763 that basalt was actually a volcanic rock, then the occurrence of columnar jointing became, at once, an infallible indicator of former volcanic activity. It thus played a major role to demonstrate that volcanism was a major geological agent and not the accidental phenomenon indicated by the existence of the limited number of active volcanoes known at that time.

Among the most famous examples are those from the Giant's Causeway in Northern Ireland. We examined under a microscope thin sections of samples taken from such a column. As may be expected from faster cooling in the vicinity of the fractures, one observes a clear increase in crystallinity from the border to the middle of a column (Figure 8). In some 10–15 cm the texture changes from a predominantly glassy matrix with only few crystallites to an almost fully crystallized rock with the same composition.

Although the manner in which columns form is not yet fully understood, the phenomenon is a striking illustration of the changes in thermal expansion that take place at the glass transition. In some respect, the phenomenon is similar to the accumulation of internal stresses within a glass piece that is not annealed. The difference here is that fractures take place in a regular way because the presence of crystals prevents them from propagating in directions parallel to the cooling surfaces. It has been found that the column radius and fracture size are proportional to each other and inversely proportional to the cooling rate of the lava [15]. The thermal expansion at the liquid–glass transition decreases more for SiO_2 -poor than for SiO_2 -rich lavas. It implies that the stress accumulated increases and, in agreement with observations, that the section of the columns decreases correspondingly.

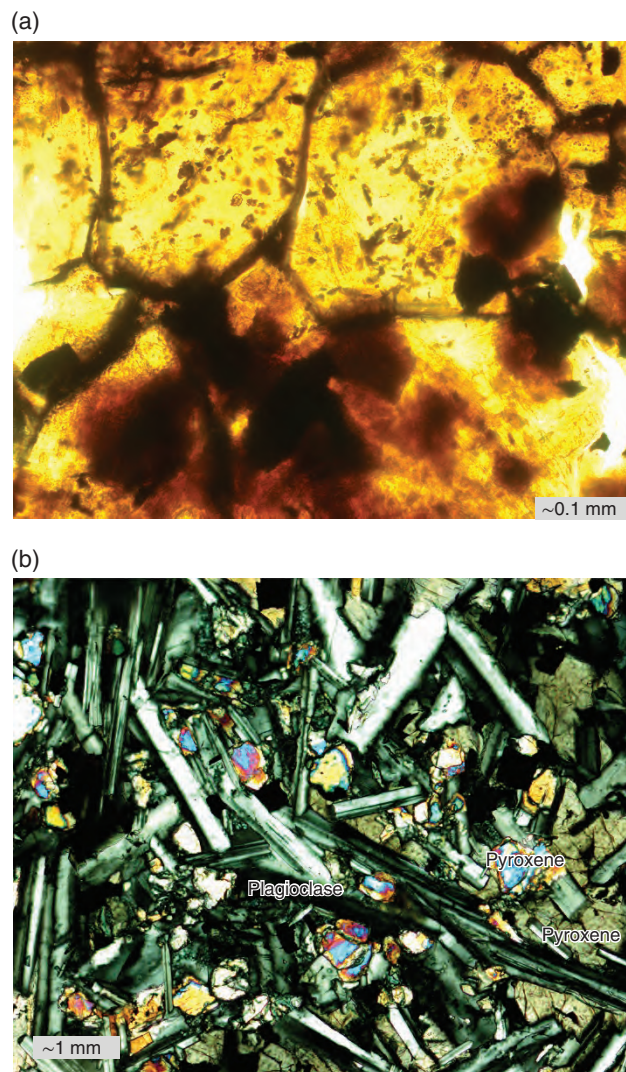


Figure 8 Crystallinity contrasts in columnar basalt as seen in thin sections cut perpendicular to the vertical axis. (a) Low crystallinity at the border of the column (photomicrograph under natural light). (b) High crystallinity near the center (photomicrograph under polarized light). Sample from the Giant's Causeway, Northern Ireland.

6 Siliceous Glasses

6.1 Pumices: Bubble-Rich Glasses

When observed under the microscope (Figure 9), volcanic products generally show void or bubbles, crystals, and an apparently glassy matrix with dark and light brown portions. The former portions contain tiny crystals, invisible under this magnification, which partially absorb light but is mostly crystal-free and therefore isotropic and translucent. In view of crystals dispersed in a

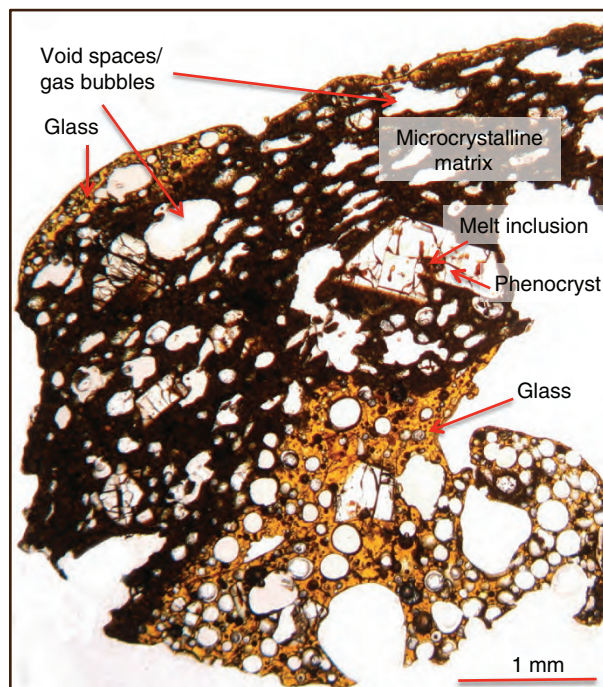


Figure 9 Coexisting crystals, glass and bubbles in a rapidly quenched lava fragment from Croscat volcano (Catalonia, Spain). Photomicrograph under polarized light C. Cimarelli.

glassy matrix, volcanic rocks might be considered as glass ceramics but of a special kind because of the presence of voids.

Among volcanic products pumices are readily distinguished by their density that can be as low as 0.7 g/cm^3 , which allow them to float on water (a feature that long ago allowed sailors exploring uncharted seas to know that some island was to be found nearby). Such low density of course originates in a very high vesicularity where voids are mostly interconnected because they represent the leftovers of the gas that was contained in bubbles before their eventual escape. Whether microcrystalline or crystal-free (Figure 9), the silicate matrix of pumices thus represents another example of glass blowing upon exsolution of volatile components during magma ascent and eruption. With respect to reticulite, the main difference is a higher magma viscosity mostly related to a higher silica contents (Table 1). Pumice formation thus points to more explosive eruption styles where vitrification is related to volatile release caused by decompression at the top of the fragmentation layer (Figure 10). Industrially, pumices are extensively used, for instance, as abrasives thanks to the sharp edges constituted by the thin walls separating

the bubbles. They are further used in agriculture, civil construction, and house building.

6.2 Obsidians

Because glass formation depends so much on cooling rate, under favorable circumstances, almost pure glasses can form as large blocks for SiO_2 contents that can be as low as about 60 wt % in special cases. This is why the term *obsidians* denotes natural glasses with a significant range of compositions. As extensively discussed in Chapter 10.1, the unique properties of obsidians made them extremely valuable before metallurgy was born. Obsidians have esthetic properties that make them valuable as ornaments. However, the most important property of obsidian is to break up macroscopically without developing straight planar surfaces but rather smooth, curved bowl-shaped surfaces, the so-called conchoidal cleavage (Figure 11). Upon magnification, however, sharp edges become visible. They have been investigated in fragmentation experiments made under controlled compressional stress regimes [4]. Newberry obsidian, from Oregon, is, for instance, flow banded on a mm scale with less than 1 vol % crystals (iron oxide microlites). Lacking both grain boundaries and a connected porosity (<2% vesicles), it gives rise upon controlled stress to sharp blade edges that do not look jagged even when observed under an electron microscope (Figure 12). Interestingly, these remain straight down to a thickness of only 3 nm, which makes them about hundreds of times sharper than the sharpest steel blade known. Hence such *Stone Age* obsidian tools are still in use for biological and medical research purposes.

The presence of microlites in obsidian has in contrast strongly detrimental effects on blade sharpness and also on uses as ornamental stones. Exceptions are *snowflake* obsidians, in which scattered flakes of white feldspathic crystals are found; *fire* obsidians, which owe their names to tiny iron oxide inclusions (Figure 11); and *rainbow* obsidians with multicolored optic effects. Like chemical composition, the nature and proportion of crystals in obsidian depend on the peculiar geophysical and thermochemical conditions under which the magma formed, evolved, and eventually cooled. Complete characterization may thus require a combination of analytical techniques such as SEM, TEM, and EDS analyses (Chapter 2.3) along with studies of cleavage, fracture, and etching patterns, which are considered to help greatly in more complex cases.

In archeological studies, what matters most is the trace element content of the obsidian because it can be highly variable even for samples coming from a relatively small

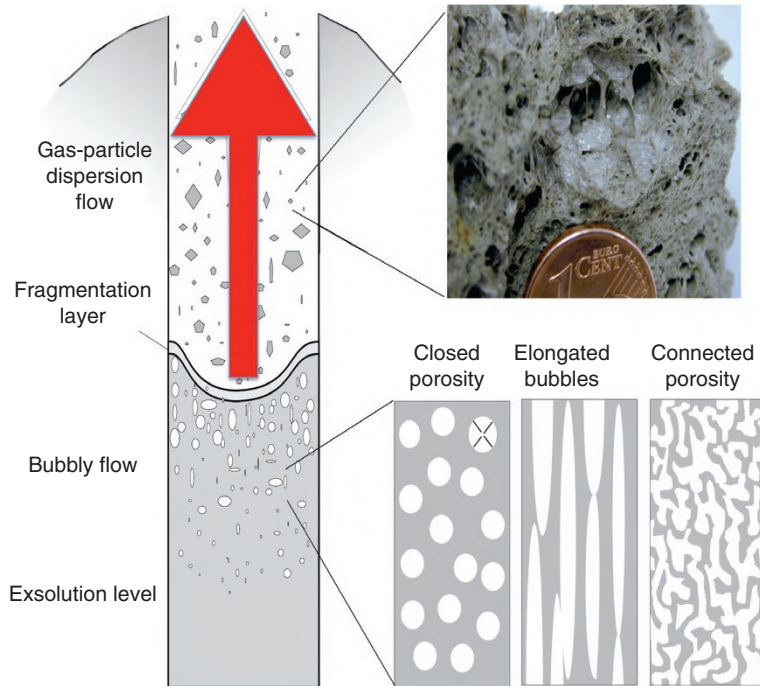


Figure 10 Bubble generation in a volcanic conduit (at the top of the fragmentation layer) from volatile exsolution induced by decompression during an explosive eruption. *Source:* Modified after S. Mueller [16].

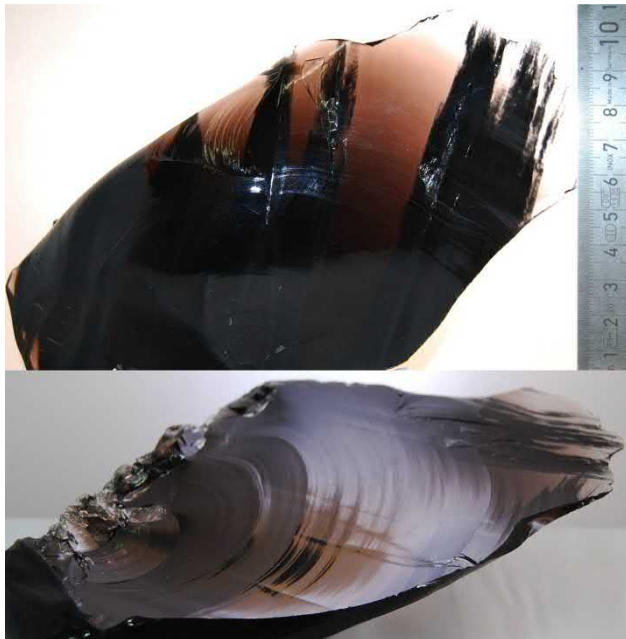


Figure 11 Obsidian from Armenia showing layering of transparent and banded obsidian (upper image) and the characteristic conchoidal fracture (lower image). Sample courtesy U. Kuippers.

geographical area (Table 2). It is this high chemical variability that allows the origins of obsidians to be tracked. Referring to Chapter 10.1 for various case studies of the provenance of prehistoric artifacts, we will present here

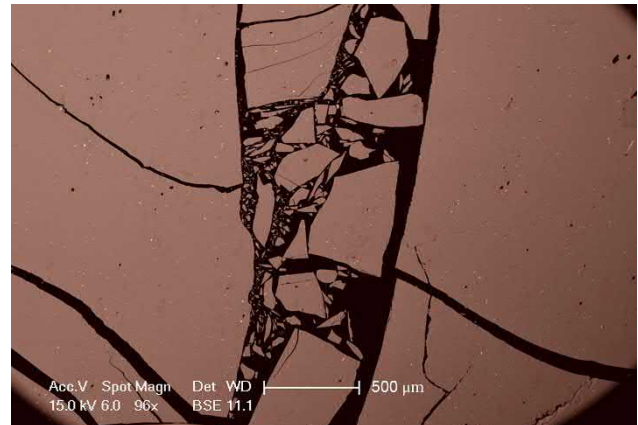


Figure 12 Blade edges from a lab compressed banded obsidian. Tiny lighter points are iron oxide microlites (<1 vol %). BSE image shows high homogeneity: no grain boundaries and lack of connected porosity (original gray BSE image from S. Kolzenburg).

the interesting example of a mosaic of the Church of St. Juvenal in Umbria (Central Italy). In fact, the obsidian tesserae of the mosaic depicting the “Majestas Christi” come from the Monte Arci deposit, in Sardinia. This material matches and has been reused from another church (the Cathedral of Narni) in the St Juvenal mosaic [17]. Such a recycling is very common in medieval artifacts and greatly complicates the dating of obsidian-crafted objects.

Table 2 Trace element composition of obsidians from Mediterranean and Near East areas [17].

	Mediterranean area					Near East
	Aegean area	Flegrean Islands	Civita di Bagnoregio	Eolie Islands	Sardinia	North Caucasus
As	7.71	21.9	24.9	18.1	12.3	12.6
Ba	542	298	613	206	271	331
Ce	46.2	170	115	161	42.1	105
Co	8.01	0.93	11.8	1.27	2.97	0.31
Cr	16.3	1.22	98.2	11.5	241	1.27
Cs	7.99	27.5	18.4	22.4	4.57	13.6
Eu	0.57	1.24	1.58	0.79	0.33	0.68
Fe %	1.52	1.88	3.86	1.89	1.39	1.78
Hf	4.59	12.3	6.23	14.0	7.07	14.1
K %	3.34	6.99	1.98	5.16	4.71	4.32
La	12.0	27.4	19.9	30.2	7.80	10.4
Na %	2.11	2.48	0.72	2.66	2.43	2.32
Nd	231	618	583	572	361	444
Ni	12.6	11.1	51.1	12.4	116	14.2
Rb	126	324	217	308	248	218
Sb	0.75	0.84	0.70	0.71	1.44	0.58
Sc	3.92	2.15	14.3	2.65	4.77	2.87
Se	2.25	7.23	1.88	8.77	7.49	6.21
Sm	3.11	9.90	8.02	10.7	6.16	7.74
Sr	100	93.3	518	26.9	9.15	16.4
Ta	0.99	4.09	1.06	4.88	3.86	3.45
Th	12.3	40.1	23.6	46.7	16.2	22.5
U	3.33	21.6	3.92	14.8	5.30	10.1
W	148	305	184	310	185	197
Yb	1.85	5.00	1.01	5.67	2.78	5.53
Zn	34.9	59.1	77.1	77.4	406	81.3
Zr	142	435	212	441	193	439

Mean element levels along maximum and minimum values of obsidian collected in different well-defined deposits and analyzed by INAA ($\mu\text{g/g}$, except Fe, K, and Na expressed as %).

7 The Fate of Natural Glasses

Lunar glasses have been preserved in a pristine condition ever since their formation billion years ago thanks to the moon's extremely dry environment (Chapter 7.1). On Earth, geological glasses are inevitably subjected to the corrosive action of atmospheric and underground agents. In this respect, an interesting feature is that, by diffusion processes, volcanic glasses can slowly dissolve small but significant amounts of water at ambient temperature and then persist in an amorphous state from tens to hundreds of million years. These glasses are then called

perlites or *pitchstones*. Although the literature on the formation process is scarce and contradictory, the current consensus is that the water content in the ground mass remains lower than 1 wt % in obsidians, whereas it is higher than 2 wt % in perlites and from about 5 to more than 10 wt % in pitchstone.

The physical boundary between obsidian and perlite is distinct and sharp as seen in the macroscopic features of "Apache's tears" (Figure 13). Perlites and pitchstones actually show a characteristic "perlite" texture, which comprises a curved or spherical crack network in the glassy matrix. The fractured glass



Figure 13 Apache tears: a perlite with obsidians inclusions from Superior, Arizona, USA. Perlites show a characteristic “perlitic” texture with a crack network in the glassy matrix. Obsidian is dark with typical shiny brilliancy. Source: Sample courtesy A. Gilg.

fragments in the cracks are often completely devitrified. Occasionally, one can in addition detect decreases in water concentration from the rim (next to the cracks) to pristine obsidian. The formation of the crack network and its subsequent hydration is interpreted as resulting from cooling of the melt in a submarine environment.

The high fracture density and surface area of perlite and pitchstone make these volcanic products ideally suited for simultaneously holding water and air pockets. This dual ability of aeration and water retention is directly put to use in various industrial applications. Like natural pumice, processed perlite and pitchstone are used as soil amendment in horticulture or as filler in the construction industry. In addition, perlite has found applications in the building industry. Upon heating, the glass transition is crossed at around 770 °C above which water exsolution and bubble growth take place to create a foamy network. The result is a very lightweight product with more than 10 times its original volume, which is used especially for insulation and as a component of lightweight concrete.

In the presence of water, the least evolved glasses (basaltic composition) devitrify in a complex manner. The end product consists of a mixture of residual basaltic glass and dominantly clay minerals, such as smectite and zeolites [18]. The contribution of microorganisms in the process is still open. The issue is important because there is evidence for glass bioalteration dating back to 3.5 billion years [14]. If it were confirmed, this result could mean that some of the earliest microorganisms used the thermodynamically unstable state of basaltic glasses

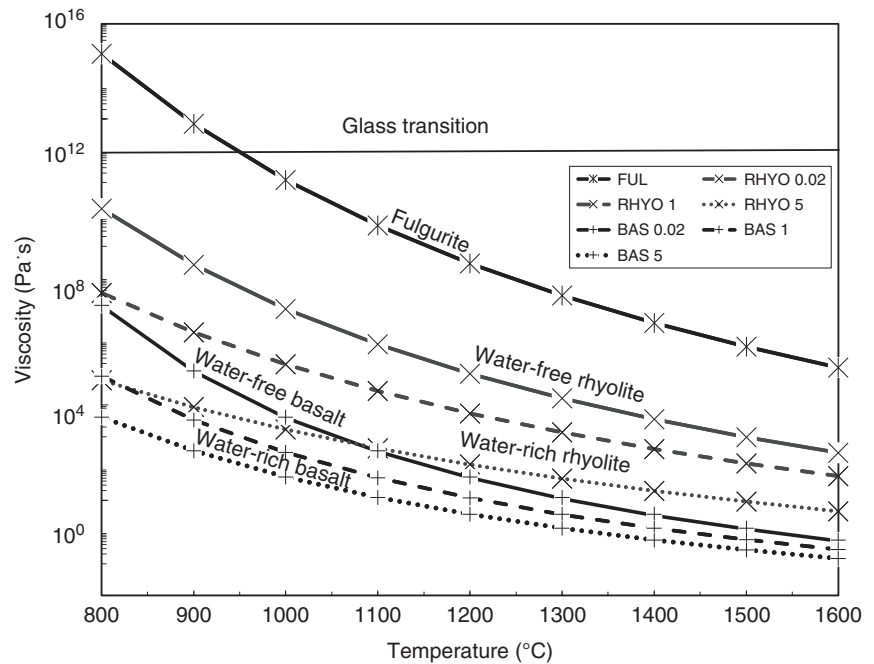
as an energy source. In this way, the glass alteration process would have constituted a foundation for very early life.

8 Compositional vs. Rheological Variability

In view of the rather simple compositional trends defined by geological glasses formed by cooling of liquids (Figure 1), it is appropriate to conclude this review with a brief discussion of *magma differentiation*. Magmas originate by partial melting of deep rocks under different conditions of temperature, pressure, and fluid content. By far the most important are *peridotites*, which are mainly made up of $(\text{Mg,Fe})_2\text{SiO}_4$ olivines and $(\text{Ca,Mg,Fe})\text{SiO}_3$ pyroxenes (cf. [13]). In mid-ocean ridges or in some continental contexts, such *primary* magmas ascend directly to the Earth’s surface as indicated by the peridotite nodules often carried up as inclusions in basalts. Upon slower ascent, however, magmas may reside for possibly long times in magma chambers where they alternatively crystallize partially first into olivines and pyroxenes. The residual liquids then become enriched in Si, Al, and alkalis so that its composition drifts from SiO_2 -poor basalt toward SiO_2 -rich rhyolite (Figure 1).

The input of new primary magma from the mantle and the coeval assimilation of enclosing rocks are additional factors changing the composition of natural melts. During emplacement up to the surface, other rocks and sediments may also be incorporated, partially melted, and merged into the original magmatic system. The interplay

Figure 14 Viscosity range (in log units of Pa·s) for natural magmas and some remelted materials. Compositions from [19]. Viscosity calculations after [20]. The upper diagram (a) shows viscosity calculations of water-free melts. The diagram below (b) shows same compositions with 1 and 5% of water dissolved in the silicate melts. Temperature in °C. Normal magmatic temperature conditions are below 1200 °C.



between all these processes, therefore, leads to coeval convection and diffusion processes (mixing) and to further complex differentiation. Primary or primitive magmas from the mantle evolve to produce the whole range of compositions presented on Figure 1, including natural glasses and the wide range of natural terrestrial volcanic rocks.

The compositional range of geological glasses is, therefore, bracketed by basalt (e.g. Pelé hair and reticulite) and rhyolite (e.g. obsidians and pumices) in (Figure 1). Intermediate glass compositions are found mainly in pumices and in matrix components of other volcanic rocks (andesite, trachyte, and phonolite). As glass ceramics, they do not exhibit the cleavage and optical properties of obsidians. If their uses remain restricted to building purposes, they are nevertheless of great interest for petrologists, who pay attention, in particular, to their glassy matrices.

The compositional evolution of magma of course translates into very large viscosity changes and thus greatly affects the glass-forming ability of the magma and its eruption style. Basaltic glasses only form under abnormally high magma production and/or high cooling rates. High rates are achieved either with water cooling in lakes or in the sea or when extensive fragmentation takes place in air and increases the surface to volume ratio. At the other end, less fluid magmas rise more slowly and thus cool down more on their way to the surface. They may reach it at temperatures of only 800 or 900 °C, at which

their viscosity can be as high as 10^8 Pa·s so that bulk vitrification becomes possible if liquidus temperatures are in addition not so high. This is actually the case for obsidians. At a microscopic level, the special properties of obsidians are related to the predominance of Q^4 species in their structure, which is thus a three-dimensionally interconnected network of SiO_4 tetrahedra.

These effects are enhanced by volatile exsolution because water depresses viscosity much more near the glass transition than at superliquidus temperatures (Chapter 5.5). In other words, the viscosity of the parent magmas of obsidians increases more quickly upon degassing and cooling than upon only cooling, which also favors vitrification (Figure 14).

Turning now to eruption styles and types of volcanic products, it is worth recalling that the driving force for explosive eruptions is ultimately linked to volatile exsolution and subsequent overpressurization of the growing bubbles during the rise of magmas toward the Earth surface. In fluid magmas, either at high temperatures or at low SiO_2 contents, bubbles travel undisturbed to the surface and escape, leaving no track behind. This efficient removal of the gas phase from the magma leads to a purely effusive and nonexplosive magma flow (Hawaiian activity). At moderate viscosity, bubble extraction and coalescence still take place, but gas slugs are generated and the cause of ash, bomb, and splatter production (Strombolian activity and lava fountaining).

In a highly viscous magma, pressure strongly builds up if the bubbles remain isolated. Upon rapid decompression on the way up, bubbles can then blow up and fragment the lava, leading to strong explosive volcanic events (Figure 10). The most explosive eruptions (Plinian, Pelean) and related products (pumices) are linked to such SiO₂-rich melt compositions.

9 Perspectives

Per se natural glasses do not have a fundamental importance in igneous petrology because they are found only in volcanic rocks, in which they are generally not the major phase. But their analysis will nonetheless continue to yield valuable clues onto the formation and evolution of lavas and thus on a variety of the magmatic processes that have shaped the Earth at all scales. In some respect, however, tektites or Libyan glass are unique since they reveal extraordinary events that had likely major consequences in the past on the biosphere and would have still more catastrophic effects if occurring in the modern world. As for obsidians, their importance in archaeometry does not need to be stressed again.

Perhaps not so well known in glass circles is the great but indirect importance that natural melts have acquired through the work consistently done by earth scientists since the late 1970s to arrive at a better understanding of structure–property–composition relationships [19], especially for viscosity and density. Given the almost unlimited natural conditions of chemical composition, temperature, and pressure, such work is not only a prerequisite for any serious petrological applications but is also valuable in a variety of industrial applications for which high-quality physical data are needed (e.g. Chapter 1.7). In addition, natural glasses are of course extremely valuable model systems in studies of long-term glass stability especially with respect to corrosion by aqueous solutions in the contexts of municipal (Chapter 9.9) and nuclear (Chapter 9.10) waste storage.

Concerning practical applications, natural glasses such as pumices and pozzolans [21] will continue to be used as inexpensive abrasive or porous materials. Their hydraulic properties are also likely to be more extensively exploited in cement production [21]. As part of volcanic rocks, natural glasses will also be more used as more environmentally friendly raw materials, for example, in the production of insulation fibers where the presence of iron is in fact required and not avoided (Chapter 9.3).

Acknowledgments

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7.3

Corrosion of Natural Glasses in Seawater

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1 Introduction

The chemical alteration of natural volcanic glasses plays a major role in controlling seawater chemistry [1] and aqueous CO_2 uptake during dissolution [2]. Of particular importance is the chemical alteration of basalt (Chapter 7.2) that makes up much of the oceanic crust. Rapid quenching of magma by seawater, in particular at mid-ocean ridges (MOR, the long submarine volcanic chains formed by upwelling magma at divergent plate boundaries), leads to the production of large volumes of basaltic glass. In fact, basalt glass comprises 20% of the extrusive layer of oceanic crust in the Atlantic [1].

Interaction with seawater results in chemical alteration of both basalt rock and glass, the latter being by far the most reactive phase because of its metastability. Given the volumetric importance and high reactivity of basaltic glass, its chemical alteration by seawater represents a key process in controlling the composition of oceans, and can even be considered as a proxy for chemical weathering of oceanic crust [1]. When altered oceanic crust is brought down into the mantle by subduction, the cycling of elements, including halogens and noble gases [3], is therefore in large part also controlled by seawater–basalt interactions. In addition, these interactions consume aqueous CO_2 [2], thereby making this process an important part of the global carbon cycle. Since basalt is rich in calcium and magnesium oxides, reaction with CO_2 -rich solutions can lead to extensive formation of Ca and Mg-carbonates, which represents permanent geological sequestration of carbon [4–6]. Basalt glass alteration is also important for industrial applications, in particular

as an analog process for nuclear glass corrosion over geological time scales [7].

In this chapter, the metabolic processes of microorganisms living in seafloor basalt environments are presented, many of which are related to reactions that lead to biologically mediated basalt glass alteration. A critical analysis of current models of biotic and abiotic alteration is then made in terms of the preferential cation leaching and coupled interfacial dissolution–reprecipitation (CIDR) mechanisms (Chapter 5.12). The first theory postulates that certain labile cations are preferentially released from the glass structure and replaced by hydronium ions (H_3O^+) from the surrounding fluid. The overall process, controlled by interdiffusion, results in the formation of a cation-leached, silica-rich surface layer. According to the second theory, these surface layers form by the contemporaneous coupling of congruent glass dissolution and reprecipitation of a hydrated silica surface layer. This is an interfacial chemical process that occurs within a thin fluid film of ordered water molecules bound to the pristine glass surface. In the first theory, the leached layer is characterized by broad sigmoidal cation depth profiles, whereas a very sharp chemical and structural interface separates the silica layer from the glass in the second theory.

2 From Basalt Glass to Palagonite

Bulk basalt glasses formed at the MOR generally have the same composition as basalt rock, being mainly composed of SiO_2 , Al_2O_3 , CaO , MgO , and FeO [8]. Another basalt glass type, called interstitial, is primarily composed of just SiO_2 and Al_2O_3 . It constitutes the matrix of crystalline phases within pillow basalts, massive flows, and dikes [8].

The first step in the chemical alteration of basalt glass in seawater at low temperatures generally results in the

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formation of *palagonite* – German *Palagonit*, from *Palagonia*, Sicily [9]. This phase is akin to a gel and appears as a brown to yellow-colored rind forming a distinct surficial layer on the pristine glass [10, 11]. Its chemical and structural complexity has been investigated by transmission electron microscopy (TEM) and nano-secondary ion mass spectrometry (nanoSIMS) [12]. Palagonite has sometimes been specifically characterized as a hydrated, cation-depleted altered glass layer, but more often is simply considered as a surface alteration product originating from the hydration and oxidation of fresh glass, which results in a porous mix of amorphous, poorly crystalline, and crystalline authigenic (i.e. formed in situ) phases. In contrast, interstitial glass alteration may not involve palagonite formation, but rather direct formation of clays [8]. The presence of palagonite between fresh glass and authigenic phases has not always been discerned, but in many cases can be attributed to insufficient analytical resolution.

Secondary authigenic minerals, such as phyllosilicates, zeolites or Fe, and Mn-oxyhydroxides, may form on the palagonite surface either from a surrounding oversaturated bulk solution or in specific cases, through in-situ transformation of the palagonite itself. In environments with elevated temperatures (up to ~400 °C), such as those found at hydrothermal seafloor vents, a different suite of secondary phases will form. In general, precipitation of authigenic minerals within pore spaces may hinder access of seawater to the fresh glass interface, thus passivating the alteration reaction [13].

3 Seafloor Basalt Alteration by Abiotic and Biotic Processes

Alteration of basalt glass by seawater occurs by abiotic and biotic processes, but their partitioning is still not well known. The roughly 200 000 km² occupied by seafloor basalts constitute by far the world's largest continuous microbial habitat [14]. It is generally accepted that microbe–basalt glass interactions control biogeochemical budgets, as well as the cycling of many elements (e.g. C, Fe; [14, 15]) between seawater, the ocean crust, and the upper mantle. Exposure of fresh basalt to seawater results in abiotic alteration and surface coverage by epilithic (surface dwelling) microbial communities. The former process produces μm-sized dissolution features (cavities, crevices, and pores) that are then rapidly colonized and exploited by endolithic (pore-space dwelling) microorganisms [16]. The ubiquitous association of Fe and Mn-oxyhydroxides with basaltic seafloor crust arguably points to the pervasive action of microorganisms.

As with abiotic alteration, biotic processes in seawater both oxidize and hydrate basalt glasses. Exposed glassy

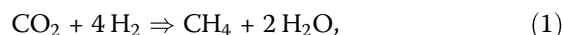
rinds of basaltic seafloor lavas on the East Pacific Rise, for example, are characterized by a distinct microbiome made of up to 10⁹ cells of Proteobacteria (88–96%) and Archaea per gram of rock [17]. This abundance is 10³–10⁴ times greater than in adjacent overlying seawater [17]. The distinct nature of basalt microbiomes is also evidenced at Arctic spreading ridges [18] and the Juan de Fuca ridge flank [19]. In general, the predominant bacterial phylum is variable and depends not only on local conditions and specific mineralogy but also on the age of the basalts [18], possibly through an effect related to the degree of alteration.

The importance of abiotic and biotic alteration is likely similar up to 90 °C [20], beyond which the survival rate of microorganisms falls off. Estimates indicate that 70–80% of all glass alteration is biologically mediated within the upper 250 m of the ocean crust, whereas this process becomes minor (<10%) at depths greater than 500 m [13].

Colonizing microbes create two principal types of micro-scale textures [21]: (i) granular clusters emanating from crack walls, characterized by 0.5–2 μm-sized nearly spherical voids that are often filled with authigenic clays and Fe-(oxy)hydroxides [13]; (ii) less commonly, worm-like tubular structures [22], a few μm in diameter and up to 100 μm in length. The latter can often have complex spiral geometries [13]. It has been proposed that biotic alteration starts with granular dissolution, which can eventually be superseded by tubular alteration [23]. Interestingly, basalt glass weathering in a subglacial environment on Iceland is also characterized by spherical vesicles, with granular clusters extending from palagonite rind into the fresh glass [24]; however, very elongated tubes and long channel structures apparently do not form.

4 Alteration Enhancement by Microorganism Metabolic Processes

Given the absence of sunlight, bacterial and archaeal assemblages in contact with seafloor basalts derive their energy from chemical reactions involving inorganic compounds, and their carbon from inorganic sources. These *chemolithoautotrophic* reactions are the basis of biomass production and microbial diversity [17]. Two principal types of metabolic chemical processes take place. The first is biotic methanogenesis [18, 19], which is mediated exclusively by Archaea with specific enzymes [25]:



where CO₂ actually exists as HCO₃[–] in deep sea environments. The source of H₂ can be either microbial or inorganic (the latter either by water radiolysis or by serpentinization reactions of olivines and pyroxenes;

[25]). Methanotrophic bacteria and Archaea will, in turn, partially consume the methane that is produced [25]. Redox reactions are the basis for the second type of metabolic process: oxidation of iron [17, 18], manganese [15], and sulfur [17]; reduction of sulfate [19], iron, and manganese [18]. Basalts are composed of minerals rich in reduced metals, such as Fe^{2+} and Mn^{2+} , as well as of minor amounts of metal sulfides (S^{-2}); all of these reduced elements can serve as electron donors for chemolithotrophic communities. Enzymes, which are macromolecular biological proteins found in cellular membranes and cytoplasm, play a pivotal role in speeding up chemical reaction rates that are vital for the metabolic activity of microorganisms [26].

The important question is how metabolic reactions of microbes chemically alter and dissolve basaltic glass. Part of the answer is that abiotic and biotic processes work in tandem, but generally at different rates. Abiotic dissolution of basalt glass under deep seafloor conditions, i.e. low temperatures and circumneutral to weakly alkaline pH conditions, is slow but nonetheless effective in releasing basalt cations, namely Si, Al, Ca, Fe, Mn, and Mg. Once released into solution (seawater), reduced metals such as Fe^{2+} and Mn^{2+} are subject to oxidization, both abiotically by oxygen and nitrate, as well as by microbial enzyme-mediated reactions [17]. The abiotic and biotic conversion of Fe^{2+} to Fe^{3+} in solution promotes iron release from the solid. In addition, a direct biotic mechanism also exists – in this case the oxidation of reduced metals is enzymatically catalyzed at the microbe–glass interface. In-situ oxidation of these metals affects their chemical bonding within the solid, thereby favoring their release and, thus, the overall dissolution of the glass. Moreover, oxidation of Fe and Mn results in the precipitation of metal-oxyhydroxides (e.g. FeOOH), which ubiquitously occur in association with basaltic ocean crust. Other prokaryotic microorganisms then use these same phases to reduce oxidized metals.

In general, biomediated redox reactions not only satisfy the energy needs of microbes, thereby allowing them to survive and reproduce, but they also speed up these reactions compared to their abiotic counterparts. The electrons liberated by the oxidation of these elements serve to reduce CO_2 , producing elemental C. The importance of microbial C fixation in deep sea floor basalts is supported by biomass calculations, which indicate that microorganisms can fix up to 5×10^{11} g of C per year, based on the assumption that the oxidation of Fe and S in the ocean crust is entirely due to microorganisms [27]. This result thus emphasizes the importance of basalt–microbe reactions with respect to the terrestrial carbon cycle.

Other types of interactions mediated by microorganisms also play a potential role in the chemical alteration

of basalt. Extracellular polymeric substances (EPS), which are mainly composed of polysaccharides and proteins, encapsulate bacteria and Archaea and allow them to adhere to inorganic substrate (rock) surfaces. They contain carboxylic acid groups that can potentially increase chemical alteration by lowering the pH at the microbe–substrate interface. In addition, polysaccharides form ligand–metal complexes in solution, which can also increase dissolution rates [16].

Microorganisms also produce (via enzymatic reactions) and secrete a variety of chemical compounds that can have a direct effect on basalt glass alteration. Chemical ligands are one such group of compounds. These ions or molecules, which form coordinated complexes with a central metal atom, bond with certain surface atoms of the solid substrate, thereby disrupting their chemical linkages and facilitating release to solution. There is an apparent positive correlation between the microbial production of organic ligands and the release rate of Si, Al, and Fe [16] from silicates. In addition to this effect, ligand complexes in solution serve to shift the solution saturation state away from chemical equilibrium, thereby increasing metal release rates from solids. Iron-specific ligands called siderophores form very strong Fe^{3+} -chelating compounds. They can bond to surface iron sites and catalyze their release to solution [15], thereby making Fe^{+3} available for eventual metabolic reactions by organisms. Enzymatic reactions also produce organic acids, which are passively or actively excreted by microbes and can also directly enhance glass dissolution. This effect is particularly effective in crevasses and pore spaces inhabited by microbes, where very low pH values have been measured, thereby theoretically increasing dissolution rates by factors of 10–1000 (e.g. pH 3.4 in pore space vs. 7.0 in bulk solution, [28]). Aside from secreted acids, dissolved microbial metabolic products are also known to be acidic in nature, and can therefore also enhance dissolution rates.

5 Biotic Corrosion Models

A generalized model of a biologically mediated corrosion processes is shown in Figure 1 [13]. The formation of granules and elongated tubes results from localized congruent dissolution by endolithic microbes that produce complexing agents, enzymes, siderophores, and acidic pH fluids. The pH in localized microenvironments is thought to be lower than in the surrounding seawater [22], and the dissolution process is assumed to be congruent, as apparently deduced from the lack of a palagonite gel. The principal alteration products are insoluble and organic matter deposited on the granule and tunnel walls,

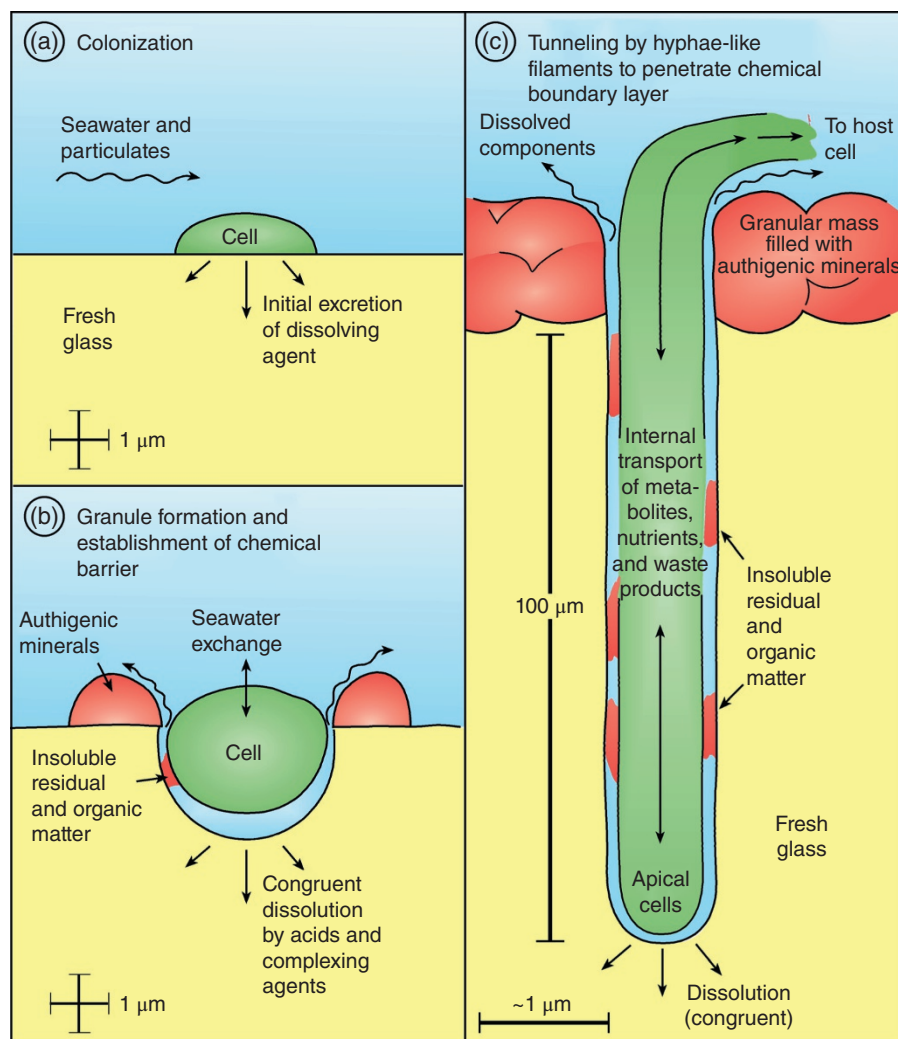


Figure 1 After the onset of colonization (panel A), biotic glass corrosion model results in granular textures (panel B) or tubular tunnels (panel C). The microbes mediate localized congruent dissolution, resulting in insoluble residual and organic matter, secondary authigenic minerals, but no palagonite. Source: Adapted from figure 14, [13].

whereas authigenic mineral phases precipitate on surfaces exposed to seawater. The tunneling action of the filamentous extension of the microbe (Figure 1c), similar to mycelium of fungi, is due to the secretion of acids and complexing agents at the tips of individual filaments. Dissolved nutrients and metabolic (waste) products are transported away from the dissolution front within the filaments themselves. Although the presence or absence of palagonite at the interface with the pristine glass (Figure 1) cannot be evaluated, this generalized model based on congruent glass alteration concurs with the CIDR model.

In the same study, alteration localized at cracks was also investigated [13]. As revealed by μm -scale elemental mapping by electron probe microanalysis, the edges of cracks from which granules originated exhibit a depletion of P, Ca, and Mg, suggesting the formation of a cation-depleted palagonite layer at the interface with the pristine glass. Mapping of tubular structures emanating from a

crack and penetrating into pristine glass was also done with synchrotron-based X-ray spectroscopy. Overall, these data point to cation loss from the glass and enrichment of other cations in regions occupied by the putative microbes. Owing to the μm -spatial resolution of these analyses, a more precise evaluation of the corrosion process is not possible.

Granular and tubular structures of assumed microbial origin have been examined at relatively high spatial resolution with TEM techniques, which include energy dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED). In a 6 Ma-old glass retrieved from east Pacific crust (Figure 2), spherical and vermicular structures extend into the fresh glass and are typically composed of 100–300 nm-wide altered glass rinds depleted in Mg, Mn, Fe, Ca, and Na, and enriched in Si, Al, Ti, and K [29]. The granular texture likely resulted from microbe-enhanced dissolution of the glass, leaving behind open tubular structures.

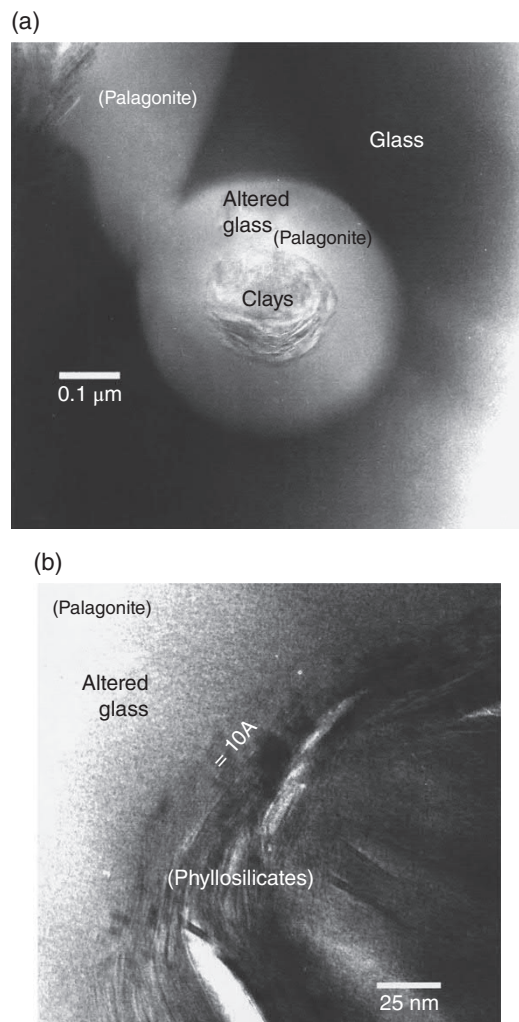


Figure 2 Putative microbial alteration of glass. (a) TEM image of glass and a spherical alteration structure composed of palagonite rim and phyllosilicate core. (b) HRTEM image of palagonite–phyllosilicate interface. *Source:* Adapted from figure 2, [29].

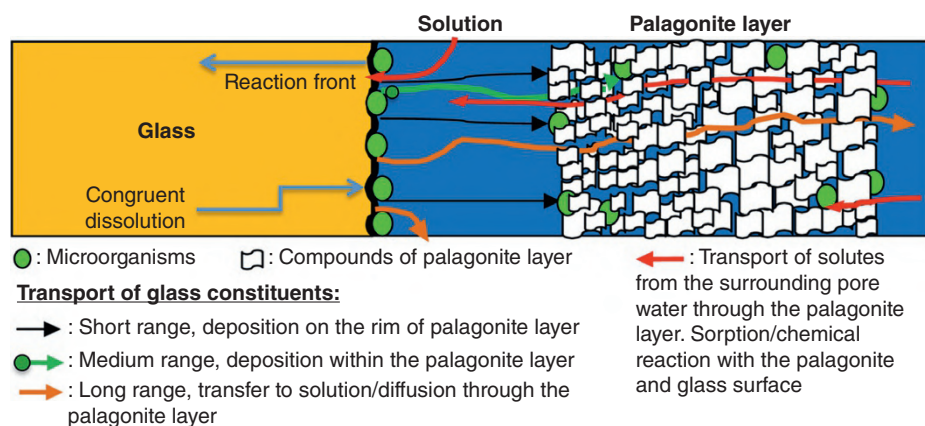
Continued incongruent dissolution of the glass led to precipitation of phyllosilicates (primarily smectite) in the open tubes, or alternatively, the smectite could have formed by in-situ replacement of the altered glass. As for the mechanisms involved, an incongruent dissolution process was suggested to yield palagonite, although the structural interfaces of palagonite with both the glass and phyllosilicate appear to be relatively sharp (Figure 2). In reality, these interfaces might have been even sharper had higher resolution imaging been achieved, thus making it possible to speculate on an interfacial reprecipitation process (CIDR). In any case, the resemblance of the spherical dissolution features attributed to biologically mediated alteration in Figure 2 with the abiotic formation of the spherical palagonite in Figure 5 is remarkable.

Other insights are possible from a study of tubules in four basalt glass samples with different provenances and ages, using various high-resolution TEM techniques [30]. With structures similar to those in Figure 2, images show the presence of fresh glass, a 20–50 nm-thick palagonite layer, and a core region containing phyllosilicates. The palagonite is depleted in Ca, Fe, Mg, K, and Mn, but enriched in Si and O, and has very sharp structural and chemical boundaries with the fresh glass and phyllosilicates at the internal and external interfaces, respectively. Without supporting or repudiating a biological origin of the palagonite present in the tubules, the authors suggested that the palagonite developed by incongruent dissolution and preferential cation leaching, followed by precipitation of phyllosilicates from a saturated solution, or by in-situ transformation of unstable palagonite [30]. Notwithstanding their interpretation, the measured Si-enrichment in the palagonite and the sharp chemical and structural interfaces agree far better with the CIDR mechanism, which would imply that the palagonite layer formed as an interfacial reprecipitate.

In another detailed study, basalt tubules investigated at the μm-scale with three synchrotron X-ray methods revealed depletion in Fe^{2+} , Ca^{2+} , and Mn^{2+} ; enrichment in Ti and Cu; and oxidation of residual iron to Fe^{3+} [31]. The tubule mineralogy is dominated by Fe^{3+} -silicates from the smectite group of clays. Whereas the biogenicity of the tubular structures remained an open question, the mechanism leading to their formation could not be unambiguously elucidated because of the insufficient spatial resolution of the analyses.

Alternatively, congruent element release and palagonite formation (Figure 3) were surmised during the chemical weathering of basalt glasses, presumably by microorganisms [32]. The palagonite occupying the tubular structures is composed primarily of insoluble Fe and Ti phases, and is separated from the glass by a gap (up to 5 μm) attributed to the pronounced loss of Si to the fluid. The physical gap [33–35] supports a CIDR process, and not preferential cation leaching. Interestingly, micrographs at the micron-scale show that the outer edges of the glass, as well as plagioclase phenocrysts, are characterized by 1 μm-thick light colored bands with distinct boundaries running parallel to the edges. These bands may in fact represent successive dissolution–reprecipitation events, but this idea would require additional work using analytical techniques with nm to sub-nm-scale resolution.

To determine the role of microorganisms in the low-temperature alteration of a 122 Ma seafloor basaltic glass, tubular and vermicular micro-channels were investigated at the nm-scale by a combination of analytical techniques, such as FIB-TEM and scanning transmission X-ray microscopy (SXTM) [36]. The micro-channels cutting through the fresh glass have 30 nm-wide Si-rich rims,

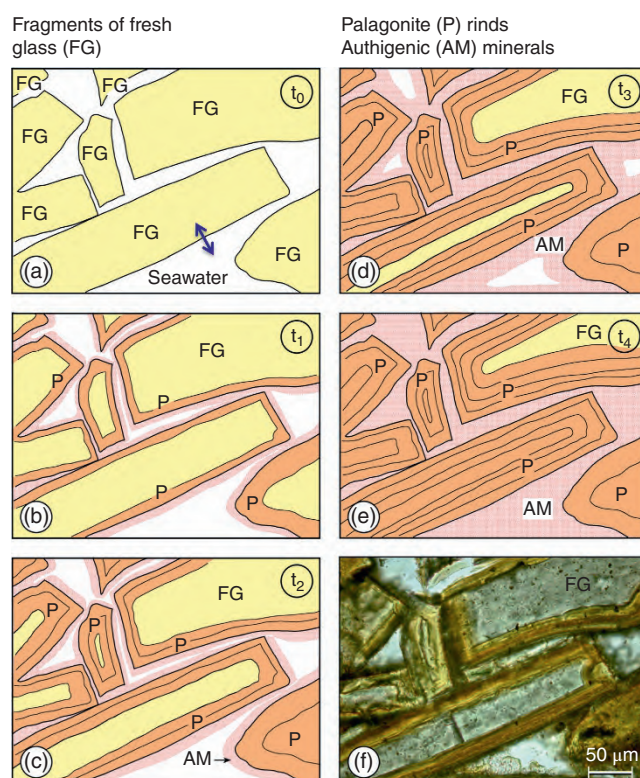


followed by palagonite with partially oxidized Fe, as well as organic carbon associated with nm-sized carbonate grains. The formation of the silica rims was attributed to incongruent dissolution and preferential cation leaching of the glass (see Figures 1–3, Chapter 5.12), which preceded the formation of the palagonite. However, two notable indices favor the CIDR mechanism: (i) the silica-rich rims have very sharp interfaces with the basalt glass and palagonite; (ii) there are abrupt, step-like changes in Si concentration between the glass and the Si-rich rim (see Figures 7 and 8, Chapter 5.12).

6 Abiotic Corrosion Models

The first step in abiotic corrosion has been stated to be hydration and chemical exchange with seawater, leading to the formation of a palagonite gel by interdiffusion of preferentially leached glass cations with chemical species from seawater, including H₃O⁺ [13]. Further alteration leads to precipitation of clays, zeolites, and iron oxyhydroxides on the palagonite gel (Figure 4). This scenario fits the interdiffusion leached-layer mechanism if the interdiffusive zone and gel are considered as the palagonite (Figures 1–3, Chapter 5.12). From high-resolution TEM images [37], the formation of palagonite was described in similar terms: incongruent glass dissolution in fracture domains leading to leached layers several tens of nm in thickness. Eventually, the Al- and Si-enriched leached layers are transformed in situ to smectite. The overall palagonitization process is characterized by a loss of Fe, Mg, and Ca, and a gain in Al, with Si enrichment being strictly restricted to the leached layer.

In a striking example of a glass alteration sequence (Figure 5a), the structural and compositional interfaces between a palagonite rind and glass are very sharp [38]. In addition, the palagonite appears to have several concentric layers delimited by sharp boundaries. A distinct



phyllosilicate layer formed at the outer palagonite interface during continued alteration. Palagonitization was associated with the creation of significant secondary porosity, and was therefore thought to involve a non-isovolumetric process – a key characteristic of CIDR [39]. Although the intrinsic mechanism of alteration

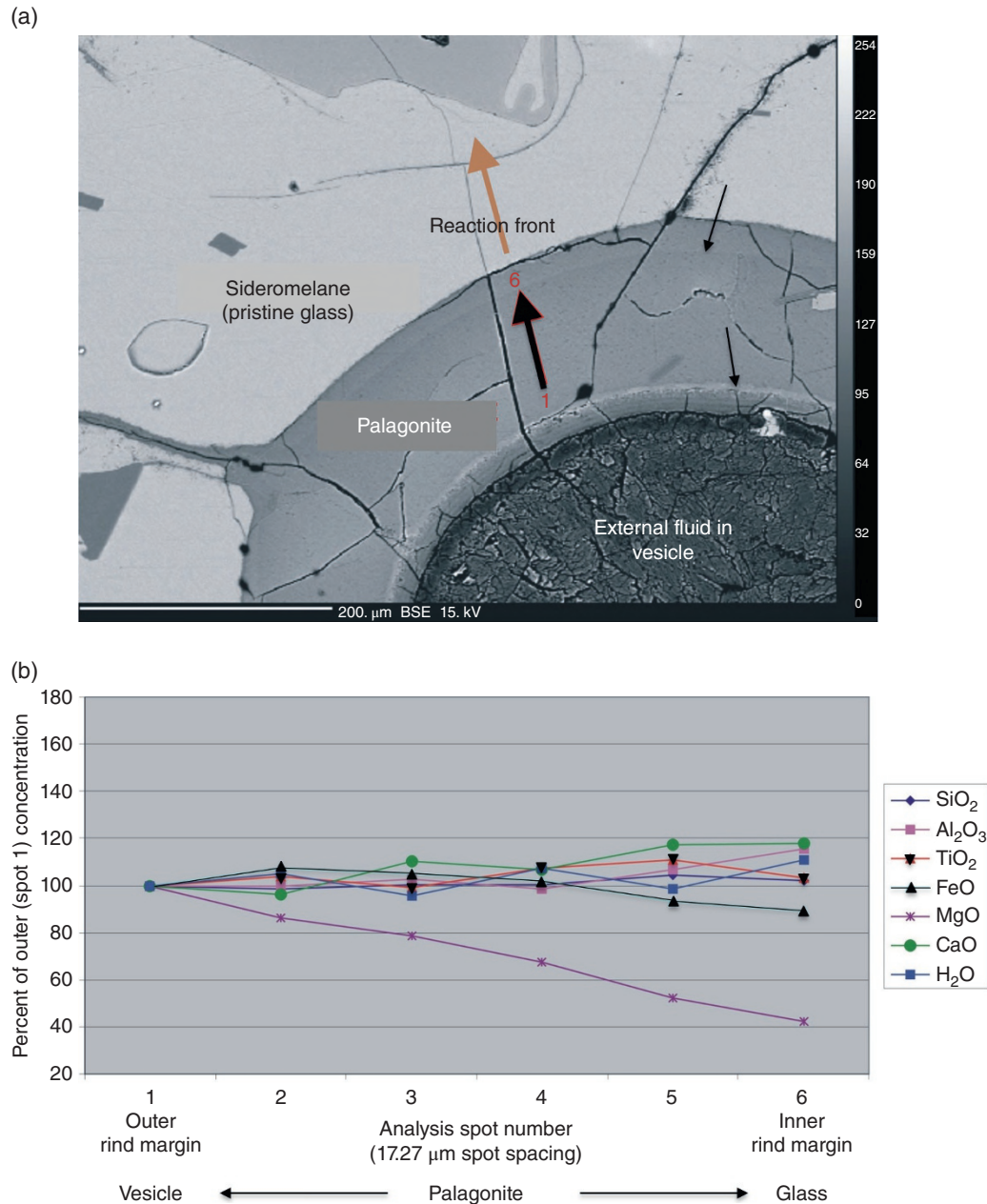


Figure 5 Alteration of sideromelane (basaltic glass) by seawater. (a) SEM image: palagonite forms by dissolution of glass at sharp reactive interface (6) – note also sharp concentric banding within palagonite (thin black arrows). (b) Chemical profiles from vesicle edge to palagonite–glass interface (1–6 arrow). Mg enrichment is a signature of seawater. Source: Adapted from figure 12, [38].

and palagonite formation was not specifically addressed, the sharpness of the glass–palagonite interface and the sharply delimited concentric palagonite layers also support the CIDR process (Figure 6, Chapter 5.12). The chemical profiles in Figure 5b cannot, however, be used to discriminate between the leached-layer and CIDR models because of their low spatial resolution.

In another model [10], the first step in volcanic glass corrosion is the formation of a yellowish-brown

amorphous gel (palagonite) rind that armors the fresh glass. The gel forms from the congruent dissolution of the glass and contemporaneous precipitation of a gel depleted in Si, Al, Mg, Ca, Na, and K, enriched in H₂O, and “passively” enriched in Ti and Fe. At the μm-scale, the sharp and distinct physical interface separating the glass from the palagonite (Figure 6) again concurs with key features of the CIDR mechanism, namely a sharp interface, congruent release of glass cations, and coupled

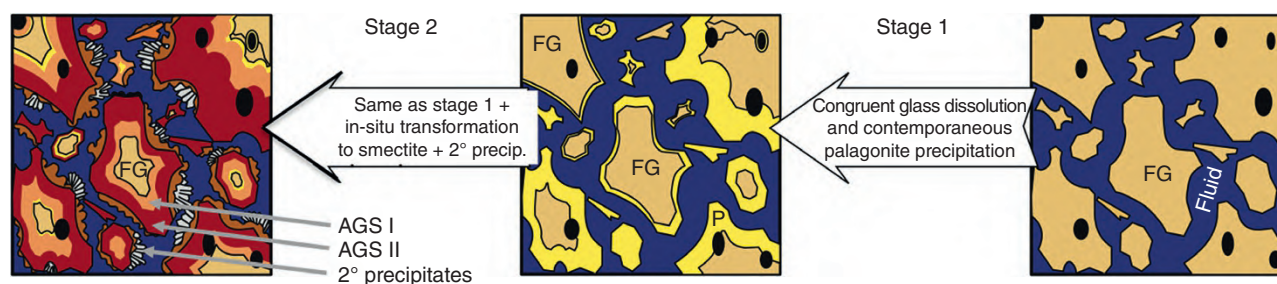


Figure 6 Corrosion of glass and formation of palagonite by dissolution–reprecipitation. Stage 1: fresh glass (FG) congruently dissolves with simultaneous reprecipitation of palagonite (P). Palagonite continuously forms at the expense of glass. Stage 2: palagonite transforms in situ to smectite (AGS I, AGS II). Secondary authigenic minerals may also form. *Source:* Adapted from figure 15, [10].

reprecipitation. Because the first-formed palagonite gel is unstable, further reaction with the surrounding fluid (seawater) results in the crystallization of smectite clays at the expense of the palagonite at its external surface (stage AGS I – Figure 6). Further alteration causes most of the remaining palagonite to be converted to smectite (stage AGS II) and other authigenic minerals.

The effect of glass composition was illustrated in a study [8] of the alteration of interstitial glasses of various ages, composed mainly of SiO_2 and Al_2O_3 , which produced an Mg-rich smectite clay called saponite. The 10 Å-lattice fringes of saponite observed by TEM in nm-proximity to the unaltered glass supports direct formation from the glass without a palagonite precursor phase, but whether there was a very thin intermediate gel-like phase between the glass and saponite is not known. If it did form at the expense of the glass via a solution-mediated transformation, then this process can be considered within the framework of the CIDR mechanism. However, saponite precipitation from an oversaturated bulk solution cannot be excluded.

In a completely different view concerning both abiotic and biotic corrosion [40], granular palagonite textures and tubular etch tunnels in basalt glass were linked to damage to the glass structure caused by radioactive decay of U and Th, which are trace elements in all basalts. Selective dissolution of alpha-recoil and fission tracks yields abiotic granular and tubular structures mimicking biotic alteration textures (Figure 7). As for the filaments that are frequently observed and often considered to be of biological origin, the authors argued that they might in fact be long tubular strands of imogolite, a secondary aluminum silicate clay mineral $[\text{Al}_2\text{SiO}_3(\text{OH})_4]$ [40]. On the other hand, certain types of complex tubular textures, such as micro-tunnels with spiral/helical, annulated, dendritic, and palmate structures cannot be attributed to dissolution of radiation-damaged glass [40], or any other known abiotic corrosion process. Nonetheless, the lack of nm-scale chemical and structural data in this study precludes identifying any specific alteration mechanism.

7 The Abiotic vs. Biotic Alteration Debate

The possibility that seafloor basalts have preserved traces of biotic chemical weathering up to 3.5 billion years old [13] is one of the most central issues concerning Earth's early evolution. This explains why studies of seawater alteration of basalt glasses have been largely devoted to the thorny issue of differentiating abiotic and biotic alteration signatures. Chemical and structural criteria have been proposed for the assignment of tubular structures to bioalteration [13]. The principal argument in favor of biogenicity is that granular, and, in particular, complex tubular structures are not likely to form from an abiotic dissolution process. In addition, chemical analyses of tubes in basalt glasses have evidenced DNA fragments and enrichment in certain elements (C, N, and P) [13]. Organisms had thus been present therein at one point in time, although there is no absolute proof that they created the actual tubes. In fact, it has been impossible to link directly specific microorganisms to granular and tubular textures found in altered glasses (e.g. [23]).

Even the use of very advanced nanometer-scale analytical techniques did not allow for the discrimination between an abiotic or biotic origin for micro-channels in ancient seafloor basalt glasses [36]. The debate is particularly tenuous with respect to putative biological tubular structures in glasses dating to the Archean (4–2.5 billion years) [13, 23, 36, 41, 42]. For example, a recent study [23] shows a convincingly close physical resemblance between tubular structures found in a fresh glass from the Troodos ophiolite and tubular structures replaced by titanite $[\text{CaTiSiO}_5]$ from the Barberton greenstone belt (metamorphosed basalts with ages up to 3.6 Ga). On the other hand, a detailed study of titanite-bearing microtubes in an Archean volcanic ash did not yield solid evidence in favor of bioalteration when examined with submicrometer-resolution methods [41].

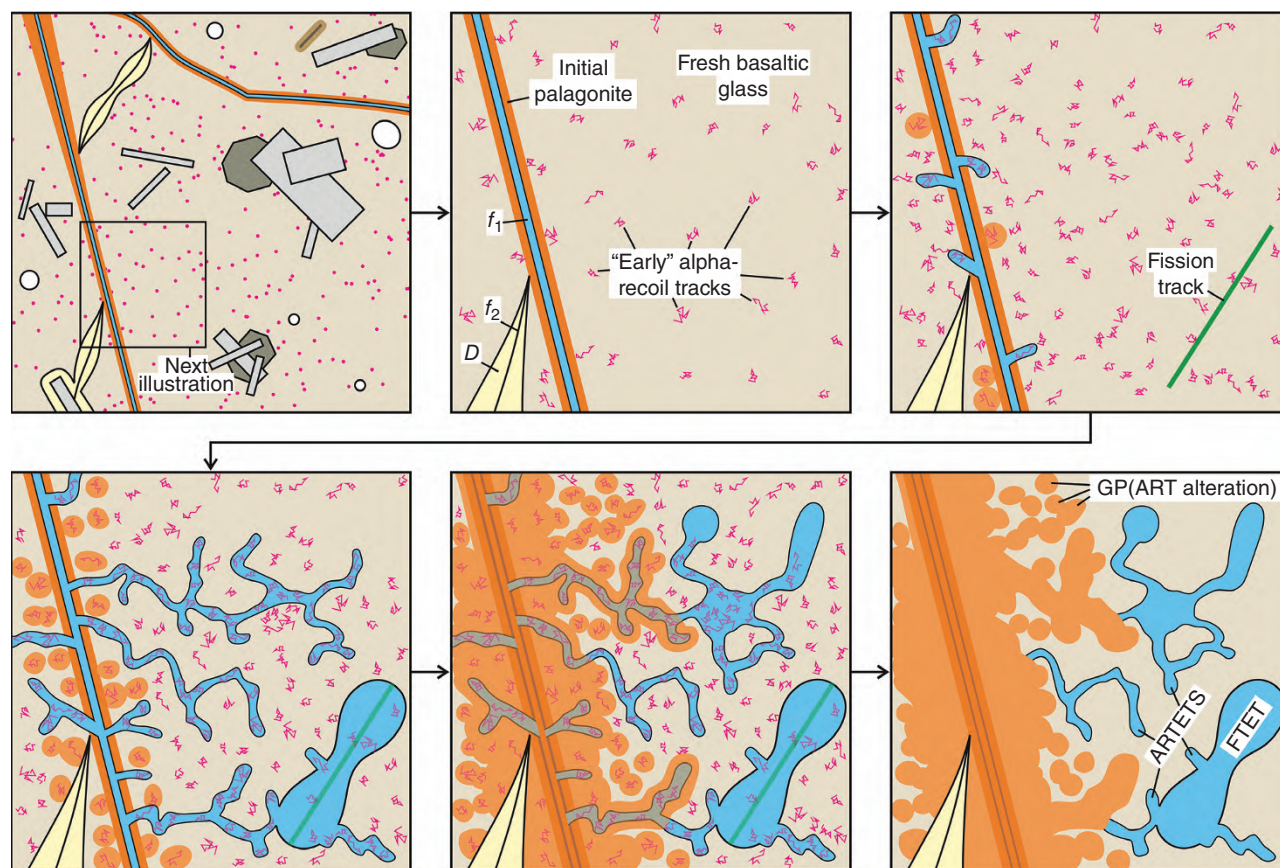


Figure 7 Abiotic corrosion of basaltic glass. Palagonite rim initially forms in a seawater-filled fracture, followed by preferential dissolution of radiation-damaged sites, resulting in complex microtextures strongly resembling biotic textures. Last panel: granular palagonite alpha-recoil track alteration (GP(ART)); alpha-recoil track etch tunnels (ARTETs); fission track etch tunnels (FTETs). *Source:* Adapted from figure 18, [40].

Adding to the debate, microbial culture studies provide evidence that bacteria growing on basalt glasses do play a direct role in the release of Si, Fe, and Mn to solution [43]; however, their overall degree of contribution to dissolution still remains largely unknown [15]. Notwithstanding, globular and tubular structures have never been replicated in the laboratory [31], but this may be simply due to the extreme slowness of biotic alteration.

8 Which Mechanism Controls Basalt Glass Corrosion?

The studies concerning biotic and abiotic alteration of basalt glasses present for the most part μm -scale cross-sectional images and chemical analyses of pristine basalt glass, palagonite, secondary authigenic minerals, and putative microbial remnants. Can these results be used to support one or the other alteration mechanism?

No single mechanism could be deduced from the abiotic group. In some studies a corrosion mechanism was not proposed [38, 40], or an incongruent dissolution/leached-layer mechanism [13, 37] was simply assumed. Others argued for palagonite formation through coupled congruent dissolution–precipitation (i.e. CIDR) [10], or direct transformation of glass into sapponite [8]. For the latter, one cannot rule out precipitation of sapponite from a saturated solution, or alternatively, transformation of a precursor palagonite into sapponite. Interestingly, hallmarks of CIDR have been reported in the abiotic group, such as Al- and Si-enriched secondary layers [37], or secondary porosity and/or sharp interfaces [8, 10, 38].

In the biotic group, the granular and tubular structures are not associated with unequivocal evidence in favor of one or the other corrosion mechanism. Whereas a specific mechanism could not be confirmed in one case [31], four others argued for initial corrosion by preferential cation release [13, 29, 30, 36]. Another investigation

[32], as well as the general model in [13], proposed congruent dissolution followed by precipitation. As with the abiotic studies, studies actually did show sharp interfaces and Si-rich glass corrosion rims that fit best with the CIDR model [29, 30, 32, 36].

Both the abiotic and the biotic corrosion studies considered the formation of secondary authigenic crystalline phases, in particular phyllosilicate minerals, in terms of two processes, namely, precipitation from a saturated solution and in-situ transformation of palagonite or fresh glass. In all cases, the authigenic minerals that occupy granular and tubular structures have very sharp interfaces with palagonite or glass, e.g. [29, 38]. Sharp chemical and structural interfaces are strong evidence for the CIDR mechanism (Chapter 5.12, see also [35, 44, 45]).

9 Perspectives

The precise molecular-scale mechanism controlling the abiotic and biotic alteration of basaltic glasses in seawater remains an open question. To date, most seawater–basalt glass studies have used analytical approaches with spatial resolutions in the μm to sub- μm -range, making it problematical to define the operative mechanism controlling alteration. Only a few studies, e.g. [30, 36], have published chemical and structural data at the nm-scale. Further progress in this field will thus certainly depend upon detailed investigations of glass alteration using more advanced, high-resolution analytical techniques. As described in Chapter 5.12, how glass samples are prepared and which analytical techniques are used is of critical importance for deciphering the molecular-scale mechanism of alteration. These tools will ultimately permit identifying the actual glass corrosion mechanism, and hopefully, may even help in the debate on deciphering abiotic and biotic alteration signatures. Of course, chemical, isotope, and structural data obtained at the nanometer scale should also be used in a complementary manner with large-scale mass balance calculations, and perhaps even be integrated into thermodynamic–kinetic models to be used as predictive tools for understanding basalt glass–seawater interactions over long periods.

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7.4

Metallurgical Slags

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1 Introduction

Metals have been a major factor in the development of human societies. This importance is illustrated by the way in which this evolution has been charted in terms of the celebrated Bronze, Iron, and Steel Ages. But the key role long played by molten silicates termed *slags* in the success of metallurgical processing is in contrast not so well known. As passed from one generation of steelmakers to the next, however, the old adage “Look after the slag and the metal will look after itself” testifies to the fundamental importance of this slag phase. In steelmaking, slags are, for instance, involved in all processes (iron making → steelmaking → primary refining → secondary refining → casting). The current steel production of about 1.6 billion tons per year thus involves more than 300 million tons of slag [1], which represents about three times the yearly glass production. And even though the figures are smaller, slags also participate in the processing of other metals such as aluminum (58 million tons p.a), silicon (8), or copper (5.5).

Metals mostly naturally occur under the oxidizing conditions of the Earth’s surface as oxides, sulfides, etc., so energy is needed to break the M–O and M–S bonds in order to reduce the oxidized forms and produce metals. This reduction can be achieved in different ways. Iron oxides are, for instance, reduced above 700 °C by CO(g) (originating in the combustion of coke or coal) in the blast furnace where 1 ton of pig iron and 0.25 ton of slag are produced by reaction of 1.6 tons of FeO_x ore with 0.45 ton of coke and 0.2 ton of CaCO₃. This *pig iron* contains about 4 wt % (or nearly 20 at. %) carbon; the C atoms sit in the interstices of the Fe matrix and

impart mechanical strength but provide little ductility (needed to obtain parts of desired shapes by rolling, extrusion, die forming, forging, etc.). Thus, steelmaking primarily consists of (i) removing carbon, which one achieves by reacting the C with O₂ flowing from a submerged lance; (ii) minimizing elements that harm the mechanical properties of steels; (iii) and minimizing *inclusions* (i.e. solid oxide particles such as Al₂O₃ or entrapped slags formed in the process), which reduce the mechanical strength of the steel.

Other reducing agents are hydrogen (from natural or water gas) or more reactive metals, for instance, Al in the aluminothermic reduction of Cr and Mn oxides. For the extremely stable aluminum oxide or hydroxide ores, electrolysis requires dissolution in an electrolyte that melts at a temperature much lower than the fusion temperature of Al₂O₃ (2050 °C). In the Hall–Héroult process, this is achieved with a cryolite [Na₃AlF₆] electrolyte to which about 4–6 wt % CaF₂ and 10–12 wt % AlF₃ are added to lower the melting point of cryolite from 1011 to 920–970 °C. Electrolysis then produces Al at the cathode and O₂ at the anode, the latter reacting with the consumable graphite electrodes to form CO(g); this provides much of the required energy for metal production. New Al₂O₃ is then added periodically to the electrolyte to keep its concentration close to the solubility limit of about 6 wt %.

Copper occurs principally in nature as mattes (i.e. sulfides such as chalcopyrite, CuFeS₂). The matte is processed in two stages: (i) oxidation of FeS according to the reaction FeS + 1.5 O₂ (from oxygen-enriched air) = FeO + SO₂(g) and then reaction of FeO with SiO₂ to form a fayalite slag (2 FeO·SiO₂), which is readily separated from the denser Cu₂S, and (ii) oxidation of Cu₂S to form blister copper, Cu₂S + O₂ = 2 Cu + SO₂(g).

Slags are critical to the success of metallurgical processing because they carry out many important tasks for

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which their physical properties must be finely tuned (Table 1). As metallurgical processes may differ widely, some of the functions of the slag are common to most of them, while others tend to be specific for a given one. The common functions include the following (key physical property of the slag indicated in brackets):

- To form a liquid slag layer that seals the metal surface from the atmosphere (liquidus temperature, T_{liq}).
- To provide thermal insulation and prevent the surface of the liquid metal from freezing (thermal conductivity, k , and porosity).
- To aid the removal of oxide and nitride inclusions from the metal (density, ρ).
- To remove elements like S, P, As, and B, which have deleterious effects on metal properties (S capacity, P capacity, etc. and T_{liq}).
- To ensure optimum heating when used in electric arc furnaces and to minimize energy costs (electrical resistivity, R).

This demand for slag properties is set to increase dramatically since these are needed as input data for mathematical models of metallurgical processes, which are now capable of identifying the mechanisms responsible for operational problems and product defects. The purpose of this chapter is to review these various issues in terms of slag properties and show how they can be now predicted as a function of the relevant parameters, of which composition is the most important. Although liquid slags are the principal focus in most metallurgical processes, the properties of solid slags are also critical in the continuous casting (CC) of steel and some other processes.

2 Basic Constraints: A Summary

2.1 Fast Kinetics

High production rates are essential in modern metal making, so any reactions involved in the process must be fast. One way of promoting fast kinetics is to maximize the interfacial area between metal and slag. In practice, one achieves this goal by creating emulsions of metal in the slag, which are promoted by the formation of slag foams; these emulsions are formed by the metal flow turbulence induced by submerged oxygen lances or by the use of high casting speeds in the case of CC (Figure 1). For example, in the basic oxygen steelmaking (BOS) process, 300 tons of molten steel are emulsified in the slag foam in less than 30 minutes. The interfacial (area/mass [or volume]) ratio of the metal drop is the key factor, which is proportional to the reciprocal of the droplet radius r . Foam stability is also important and is promoted by low values of slag surface tension (γ), high viscosity (η), and high liquidus temperature (T_{liq}) since solid particles retard slag drainage rates and therefore stabilize the foam.

2.2 Slag/Metal Entrapment

One consequence of producing metal emulsions in the slag is the loss of metal yield. This problem is especially important in the production of precious metals and of copper. Similarly, in the continuous casting (CC) of steel, turbulent metal flow causes entrainment of slag droplets in the metal. Slag inclusions reduce the mechanical strength of the steel. Entrapment can occur by a variety of mechanisms, for instance, by that shown in Figure 2

Table 1 The required functions of the slag and important physical properties and approximate composition: A = Al_2O_3 ; C = CaO; F = FeO; FI = CaF_2 ; M = MgO; Mn = MnO; N = Na_2O ; and S = SiO_2 .

Process ^a	Process aim	Slag function (slag properties)	Slag composition
Fe-BF	$\text{FeO} + \text{C} = \text{Fe} + \text{CO}$	Minimize impurities	CSAM; (C/S) = 1.1
BOS	$\text{C}_{\text{Fe}} + \text{O}_2 \rightarrow \text{CO}/\text{CO}_2$	Fast kinetics foam (γ ; η , T_{sol})	CAFS-high (C/S)
EAF	Melt scrap; de-C Fe	(S_{cap} , P_{cap}) foam for heat transfer (γ , η , T_{sol})	CAFS-high (C/S)
Ladle refining	Remove (O,S,P, Al_2O_3) from steel	(S_{cap} ; P_{cap} ; T_{liq})	CSFMA-high (C/S)
CC (steel)	Solidification-Fe	Control of heat flux and lubrication (η , T_{sol} , f_{crys})	CSNFIA (C/S $\approx$ 1);
Cu-prod'n	$\text{CuFeS}_2 + \text{O}_2 \rightarrow \text{Cu} + \text{FeO} + \text{SO}_2$	Slag is reaction medium	F_2S
Al prod'n	Electrolysis; $\text{Al}_2\text{O}_3 + \text{C} \rightarrow \text{Al} + \text{CO}$	(T_{liq} ; R , Al_2O_3 solubility)	$\text{Na}_3\text{AlF}_6 + \text{CaF}_2$
Si refining	Remove B from Si	(B_{cap} , T_{liq})	CSA
Fe/M*	$\text{Fe}/\text{M}^*\text{O} + \text{C} = \text{Fe}/\text{M}^* + \text{CO}$	(R , γ_{ms} , η)	SCM*A
M* = Cr;Mn			
ESR	Remove S, P, and Al_2O_3	(R , γ_{ms} , η)	>50%FI + CA
Smelting	Retrieve valuable metal	Minimize slag entrapment (γ_{msl} , η , [$\rho_{\text{m}} - \rho_{\text{sl}}$])	CSA

^a BF, blast furnace; BOS, basic oxygen steelmaking; CC, continuous casting; (C/S), basicity; EAF, electric arc furnace; ESR, electro-slag refining.

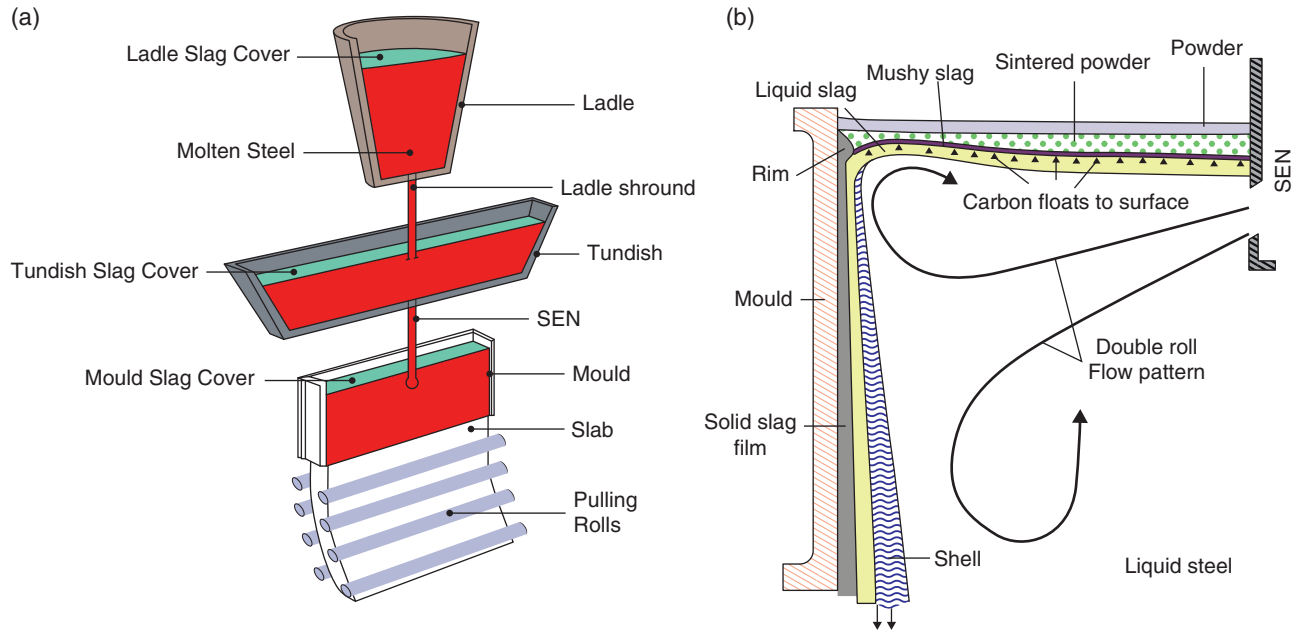


Figure 1 Sketch of the continuous casting process. (a) Ladle, tundish, and mold and secondary cooling. (b) Half-section of the mold showing mold powder added to the top forming a liquid slag pool, which, in turn, forms solid and liquid slag layers by infiltrating between the steel shell and water-cooled copper mold.

from the formation of vortices in the slag [2]. One can minimize it by using slags with high values of both viscosity and slag/metal interfacial tension (γ_{ms}). Metal entrainment in the slag can also be reduced with low values of slag density (to promote removal) and high values of γ_{ms} .

2.3 Refractory Protection

A serious problem in metal production is refractory erosion, especially when turbulent metal flow is involved, to the point that some processes have been abandoned because erosion rates were too high. One technique used to extend refractory life is to create *freeze linings*; these are formed by water cooling of the refractory and covering of the hot face with a consumable layer of solidified slag so that the freeze lining protects the refractory from erosion. For example, at the end of the BOS process, the lance used in the oxygen blow is lowered, and liquid slag is splashed to cover the refractory walls (this is referred to as *slag splashing*). The resulting slag coating protects the refractory from the turbulent metal and slag flows in the next heat. Refractory lives of more than 50 000 heats have been achieved in this way. However, for successful splashing, it is important that the slag have a FeO content of ca. 13 wt % (for good adhesion to the refractory) and contains more than 8 wt % MgO to ensure the formation of a high melting phase leading to a low consumption rate. Freeze linings are consumable, however, and do give rise to slag inclusions in the metal.

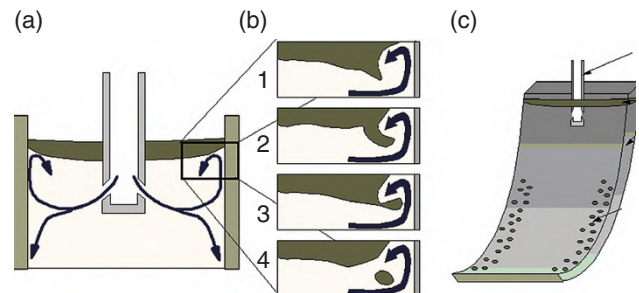


Figure 2 Sketch of slag/metal entrapment. (a) Metal flow pattern in the mold. (b) Necking and detachment mechanism for the entrapment of slag in metal. (c) Location of slag inclusions on slab arising from this mechanism [2].

2.4 Electrical Conduction

Electric arc furnaces are used in smelting and refining operations. Because the heat for the process is usually generated from the arc struck in the slag phase, the composition of the latter is selected on the basis of its electrical resistivity (R , since the energy supplied is given by I^2R). This property is a key factor in this context. In electric arc furnace steelmaking, foaming slags are used to improve heat transfer from the arcs to the metal phase.

2.5 Heat Transfer

In continuous casting, molten steel flows from a submerged entry nozzle (SEN) into the mold (Figure 2) and freezes against the water-cooled copper wall to form

a shell [3]. Two precautions are taken to prevent the shell from sticking to the mold, namely, (i) the mold is oscillated vertically, and (ii) a casting powder is added to the top of the mold where it forms a liquid slag pool from which slag infiltrates between the shell and the copper to form a film (Figure 2). This film consists of two layers, one solid ($d_s = 1\text{--}2$ mm thick) and the other liquid ($d_l = \text{ca. } 0.1$ mm thick). Serious defects in the cast steel occur if the heat transfer from the shell is not optimal. The principal factors affecting horizontal heat transfer are (i) the thickness of the slag film, which is controlled by the solidification (or break) temperature, T_{br} , of the slag, and (ii) the fraction of crystalline phase in the film, f_{crys} , which also contains a glassy phase, because the conduction of heat by radiation (k_R) decreases as f_{crys} increases [3].

2.6 Lubrication

The friction force (F) exerted on the steel shell formed in continuous casting (Figure 2b) is given by $F = A(V_m - V_c)\eta/d_l$ where A is the surface area of the mold and V_m and V_c are the velocities of mold and shell, respectively. Thus friction forces increase with increasing viscosity (η) and decreasing liquid film thickness (d_l).

3 From Composition to Reactivity

3.1 Compositions of Metallurgical Slags and Fluxes

Because of the specific needs of metal production processes, slags cover a wide range of compositions (Figure 3). These are also summarized in Table 2 where the principal functions and important properties of slags

used in iron making and steelmaking and copper, aluminum, and silicon production are also listed. Although these compositions are related to those of glasses and coal ashes (Chapter 9.9), as shown by the pseudo-ternary diagram of Figure 3, they are distinctly different in view of their lower SiO_2 and Al_2O_3 contents. Slags are low-viscosity, highly basic melts, which is not at all accidental since the former property is beneficial for rapid processing and the latter is required to remove sulfur and phosphorus whose effects on metal properties are deleterious: although the former improves machinability and the latter slightly improves strength and hardness, both reduce the ductility and impact strength and weldability of cast

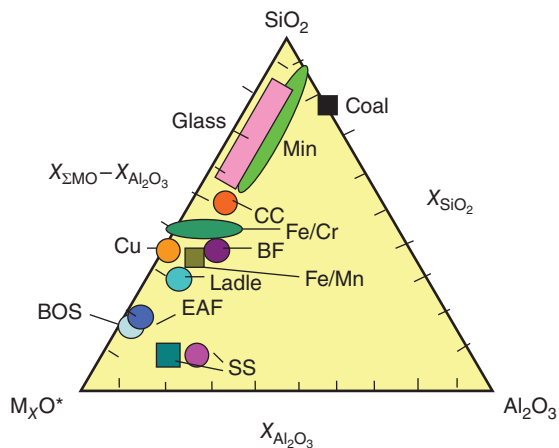


Figure 3 Composition ranges for metallurgical slags shown as a ternary diagram of mole fractions of SiO_2 , Al_2O_3 , and M_xO^* , where $X_{\text{M}_x\text{O}^*} = X_{\text{M}_x\text{O}} - X_{\text{Al}_2\text{O}_3} = \Sigma(X_{\text{CaO}} + X_{\text{MgO}} + X_{\text{FeO}} + X_{\text{MnO}} + X_{\text{Na}_2\text{O}} - X_{\text{Al}_2\text{O}_3})$, i.e. network-modifying oxides after charge balancing of Al_2O_3 ; Min = minerals; BF = blast furnace; Cu = copper making; Fe/Cr and Fe/Mn = ferroalloys; SS = secondary (refining) steelmaking slags.

Table 2 Typical compositions for slags from different processes.

	CaO	SiO ₂	Al ₂ O ₃	MgO	FeO _x	MnO	Na ₂ O ^a	CaF ₂	Others
BF slag	42	34	13.5	7.5	0.5	0.3	1		S, 1
BOS	35	14	5	8	29	7	1		
EAF	33	11	5	7	26	6	1		
Ladle ref	48	15	14	15	1.5	1	1		
CC	36	23	8 ^b	4	1	1	9	13	
Cu making	4	32	3	2	53				Cu ₂ O, 2; S, 2
Al(Hall–Héroult)			8					7.5	Na ₃ Al F ₆ , 80 AlF ₃ , 4.5
ESR	15		15					70	

^a Contains K₂O and Li₂O.

^b Contains 4% Al₂O₃ pickup from slag/metal reactions.

NB: The variability of ores leads to variations in slag compositions.

BF, blast furnace; BOS, basic oxygen steelmaking; CC, continuous casting; EAF, electric arc furnace; ESR, electro-slag refining.

iron. The viscosity of slags is also lowered by the fluxes incorporated to reduce the liquidus temperatures. The most common are CaF_2 , B_2O_3 , and Na_2O . Boron is considered a harmful impurity in both steel and silicon, whereas CaF_2 levels have been reduced in recent years in metallurgical slags to meet environmental concerns.

3.2 Reactivity of Slags

Ranging from the *docile* to the *hostile*, the reactivity is a key factor in the selection of a slag composition. In this respect, the ionic nature of slags is a fundamental feature because reaction with the metal involves the transfer of electrons (e.g. $2\text{Al}_m + 3\text{Fe}_{\text{sl}}^{2+} = 2\text{Al}_{\text{sl}}^{3+} + 6\text{Fe}_m$, where the subscripts m and sl denote the metal and slag phases, respectively). The reactivities of slag components can be ranked by use of Ellingham diagrams (Figure 4) in terms of the chemical stability of component oxides (Chapter 5.6). Stable oxides with highly negative Gibbs free energies (ΔG) are located toward the bottom of the figure (e.g. CaO), whereas less stable ones (e.g. FeO) are sited near its top. Reactive metals (e.g. Al in steel) will take the oxygen away from less stable oxides (like FeO) located above them in the figure. Thus slags containing high contents of FeO and Cu_2O tend to be unstable and very reactive.

The reactivity also increases with temperature, so slags used in metal processing tend to be more reactive when melting at higher temperatures. In laboratory experiments it is customary to contain oxides (i.e. slags) in metals and vice versa. In industrial processes, the vessel is usually lined with refractory oxides (i.e. stable oxides located near the bottom of Figure 2) since (i) these are less

reactive and (ii) these have high melting temperatures as a result of their strong M—O bonds.

Refractory erosion is a serious problem for the metallurgical industry as slags readily dissolve oxides since they are themselves oxides. The erosion rate is particularly severe around the metal/slag interface, which is known as *slag line erosion*. Here, erosion is caused by the formation of vortices in the meniscus region of the slag from dissolution of refractory oxides, which creates a surface tension gradient and results in a Marangoni surface flow from low to high surface tension [4].

Modern refractories consist of a mixture of oxides and carbon because the carbon particles alleviate the thermal stresses produced. A different mechanism causes their erosion [4]. Metals are wetting carbon but not oxides, whereas slags are wetting oxides and not metals. When the refractory surface consists mostly of carbon particles, the metal advances, covers them, and subsequently dissolves them. As a result, the surface mainly consists of oxide particles, so the metal recedes, and the slag covers the oxide particles and dissolves them until the surface is primarily made up of carbon particles. The cycle then starts over again.

The main driving force for dissolution is the concentration gradient ($C_{\text{sat}} - C_{\text{proc}}$) where the subscripts refer to the concentrations at the saturated limit and actual level in the process. In some processes, one minimizes refractory erosion by increasing C_{proc} close to the C_{sat} level.

4 Slag Properties

4.1 General Features

As already emphasized, the ability of the slag to perform its required functions in metal processing relies heavily on its properties. In Table 3, their values are, in turn, closely related to the structure of the slag, which tends itself to be dominated by its degree of polymerization at high temperatures. With respect to the properties considered, however, the strength of this relation is in the hierarchy: viscosity (η) > diffusion coefficient (D) $\approx$ electrical conductivity (κ) > thermal conductivity (k) > thermal expansion coefficient (α) > density (ρ) > heat capacity (C_p). The two other principal factors affecting both structure [5–7] and physical properties [8, 9] are the nature of the cations and temperature.

4.2 Polymerization of the Slag

That the degree of polymerization is an important parameter is clearly illustrated by the increases of viscosity with the size of the elementary structural units of the melt (Figure 5) and, especially, by the dramatic increase

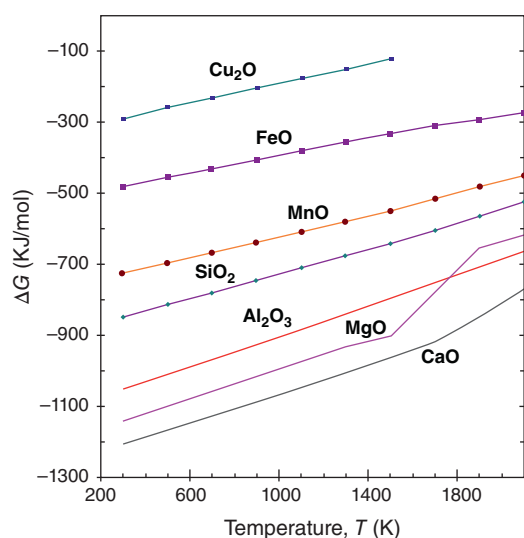
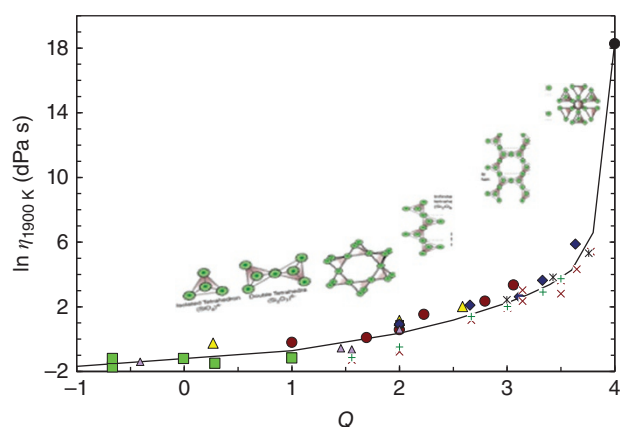


Figure 4 Ellingham diagram: Gibbs free energy of the reactions $\text{M} + \text{O}_2 = \text{M}_x\text{O}_2$ for various component oxides as a function of temperature.

Table 3 Comparison of approximate property values at specified temperatures for various metallurgical slags with those reported for molten minerals and coal ashes; □ = estimated value.

Property (Q)	BOS (<0)	BF (2)	CC(1.8–3.2)	Basalt (3.1)	Rhyolite (4)	Coal ash (4)
$\eta_{1900\text{ K}}$ (dPa s)	0.2–1	1–3	0.1–5	4–7	100–300	100–200
$\kappa_{1900\text{ K}}$	5	0.4–0.8		0.2–0.6	0.3–0.6	0.01–0.02
$\ln D_{\text{Ca}1900\text{ K}}$	–[20.5]	–[21]	–[21–22]	–22	–26	
$k_{1000\text{ K}}$	—	1.55	1.65–2	1.8	1.7	1.8
$\rho_{1900\text{ K}}$	2050	2720	2500	2700	2400	2550

**Figure 5** Values of $\ln$ viscosity (dPa s) at 1900 K for various silicates and aluminosilicates as a function of the polymerization parameter Q ; individual symbols refer to different cations; structures from left (i) single tetrahedra, (ii) double tetrahedra, (iii) three-membered rings, (iv) single chains, (v) double chains, (vi) sheets, and 3-D structures [9].

observed when 3-D structures begin to form. Several parameters have been used to characterize the polymerization of slags. Some of them are indirect measures, like the *basicity* (expressed as the CaO/SiO_2 ratio) and the *optical basicity* (Chapter 5.7), which characterizes the electron donor power. Others are defined in terms of basic structural units, namely, bridging (BO, denoted by O°), nonbridging (NBO, O^-), and free (FO, O^{2-}) oxygens, along with tetrahedrally coordinated cations (T), and yet another is very simply the *viscosity*.

The degree of polymerization is often defined in terms of two simple composition parameters. As discussed in more detail in Chapter 2.6, the first is

$$\frac{\text{NBO}}{T} = \frac{\sum 2(X_{\text{MO}} + X_{\text{M}_2\text{O}} - X_{\text{Al}_2\text{O}_3})}{(X_{\text{SiO}_2} + 2X_{\text{Al}_2\text{O}_3})}, \quad (1)$$

where X denotes a mole fraction. As to the second parameter, it is simply

$$Q = 4 - \frac{\text{NBO}}{T}. \quad (2)$$

Both parameters are modified basicities providing measures of depolymerization and polymerization, respectively. Alternatively, the numbers of BOs, NBOs, and FOs have also been used, or those of the Q^n species derived from spectroscopic experiments (Chapters 2.2 and 2.4). When relating NBO/T and Q to structure and properties, however, the big problem is that these parameters do not differentiate between different cations. Optical basicity (Λ) was introduced as a remedy (Chapter 5.7), but it predicts wrong trends for the viscosity ($\eta_{\text{M}_2\text{O}-\text{SiO}_2}$, in hierarchy $\text{K} > \text{Na} > \text{Li}$ but Λ gives a reverse trend). Until recently, a cell model [10] was required to calculate the numbers of BOs, NBOs, and FOs, but a new model to determine these parameters has become available and offers exciting opportunities [11].

In spite of its shortcomings, the parameter Q has been adopted here as a convenient way to represent the degree of polymerization (Figure 6). It should be noted that most metallurgical slags have Q values ranging from 0 to 2, whereas glasses, minerals, and coal ashes generally have Q values higher than 3. One consequence is that a property such as viscosity shows much more variation with structure, as represented by Q , for glasses, minerals, and magmas than for metallurgical slags (Figure 5).

4.3 Effect of Cations on Properties and Structure

The Si^{4+} cations are mostly arranged in fourfold coordination (denoted $^{(4)}\text{Si}^{4+}$). The network-modifying cations are often arranged in sixfold coordination in an octahedral array [5–7 and Chapters 2.1, 2.2, and 2.4]. However, on occasions there may be deviations in the coordination number (N_{coord}), which tends to increase with increasing cation size [6, 7]. The structure is also affected by the nature of the cations (illustrated by the scatter in viscosities plotted in Figure 5) although the effect is much smaller than that of polymerization.

The *field strength* of the cation, given as z/r^2 where z and r are the charge and radius of the ion (Chapter 2.4), is used as a measure of the effect of a cation on both

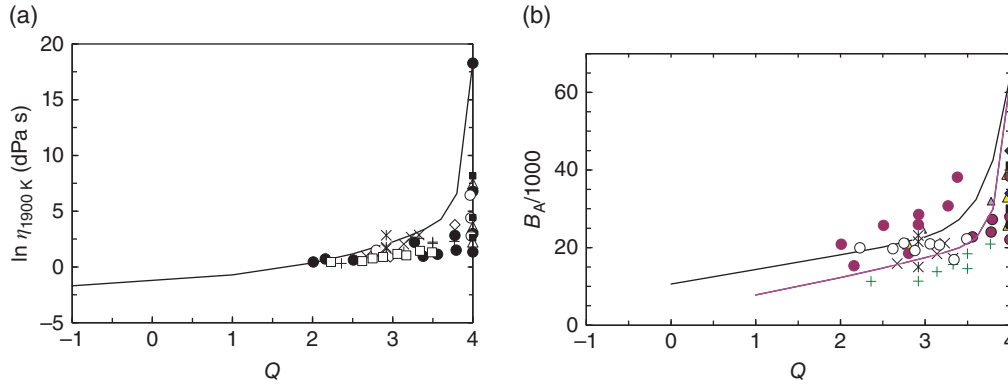


Figure 6 Effect of the polymerization parameter Q on viscosity. (a) Values of $\ln \eta_{1900 \text{ K}}$. (b) The parameters B_A . Curves, silicates; individual points, aluminosilicates. B_A curves higher for MO-SiO_2 than for $\text{M}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ systems [12].

silicate structure and slag properties. Increasing cation field strength results in the following structural changes [6–8]:

- A wider distribution of polymeric species (Q'').
- A lower coordination number (N_{coord}), which, in turn, affects the numbers of BOs and NBOs present.
- A more compact distribution of intertetrahedral bond angles (Si–O–Si or Si–O–Al in aluminosilicates), which affects the amount of disorder present (i.e. configurational entropy).
- An increasing attraction for NBOs (e.g. $\text{Mg}^{2+} > \text{Ca}^{2+}$).
- A lower probability of charge balancing tetrahedrally coordinated Al^{3+} (Chapter 2.4), which is preferentially done by the cations with the lowest z/r^2 .

5 Transport Properties

Some physical properties vary more than others with the structure of the slag. They are discussed below in the order of decreasing dependences.

5.1 Viscosity

Viscosity is the resistance to the flow of one layer of the liquid over another (Chapter 4.1). Large silicate units make the bond exchanges involved in viscous flow more difficult, so the viscosity increases, whereas the effects of the nature of network-modifying cations are much smaller (Figure 5). In metallurgy, the Weymann equation has been used to account for the temperature dependence of viscosity:

$$\eta = A_W T \exp\left(\frac{B_W}{T}\right), \quad (3)$$

where A_W and B are constants. However, Arrhenius and Vogel–Fulcher–Tammann (VFT) equations (Chapter 4.1) are more commonly used for the stable and supercooled liquids, respectively. The former is

$$\eta = A_A \exp\left(\frac{B_A}{T}\right) = A_A \exp\left(\frac{E_\eta}{RT}\right), \quad (4)$$

where A_A is a pre-exponential term, E_η the activation energy for viscous flow, and R the gas constant. With the extra fit parameter T_o , a VFT equation is selected for the supercooled domain, for instance, in solid slag films formed in continuous casting, especially those used to cast billets:

$$\eta = A_V \exp\left[\frac{B_V}{(T - T_o)}\right]. \quad (5)$$

From plots of viscosity against the structural parameter Q (Figure 6), it appears that:

- Values of $\ln \eta_{1900 \text{ K}}$ are in the order $\text{K} > \text{Na} > \text{Li}$, i.e. $\ln \eta_{1900 \text{ K}}$ increases with increasing cation size (or decreasing field strength $[z/r^2]$), but the analogous trend is less clear-cut for MO silicates, which approximates to $\text{Mg} > \text{Ba} \approx \text{Sr} \geq \text{Ca}$.
- Both the viscosity ($\ln \eta_{1900 \text{ K}}$) and the activation energy term (B_A) are very dependent upon structure (Figure 6), in a way that can be expressed as double-exponential equations for the following systems:

$$\begin{aligned} \text{MO} + \text{M}_2\text{O} - \text{SiO}_2 : \ln \eta_{1900 \text{ K}} = & -2.16 + 0.828 \\ & \exp\left(\frac{Q}{1.794}\right) + 2.19 \times 10^{-16} \exp\left(\frac{Q}{0.1036}\right), \end{aligned} \quad (6)$$

$$\begin{aligned} \text{MO} - \text{SiO}_2 : B_\eta^* = & -795831 + 8.48 \times 10^{-6} \\ & \exp\left(\frac{Q}{0.261}\right) + 795841.4 \exp\left(\frac{Q}{211587}\right), \end{aligned} \quad (7)$$

$$M_2O - SiO_2 : B_{\eta}^* = -24.6 + 6.12 \times 10^{-13} \exp\left(\frac{Q}{0.1258}\right) + 28.5 \exp\left(\frac{Q}{7.7}\right), \quad (8)$$

where $B^* = B/1000$ and η is in dPa s [12].

- iii) Values of B_A are higher for MO than for M_2O silicates [12].
- iv) Values of $\ln \eta_{1900\text{ K}}$ and B_A for aluminosilicates are lower (for $Q > 2.8$) than for silicates (Figure 6). These departures, $\Delta \eta_{1900\text{ K}}$ and ΔB_A , increase with the ratio $[2X_{Al}/(X_{Si} + 2X_{Al})]$, a trend that may be due to weaker bonding for Al—O than for Si—O bond or to the formation of AlO_5 species (Chapter 2.4).
- v) At high Al_2O_3 contents, cations are needed to charge-balance Al^{3+} ions in tetrahedral coordination; the viscosity is at a maximum when the ratio $(X_{Al_2O_3}/X_{\Sigma X_{MO}}) \approx 1$ [7, 8], but such situations are rare in metallurgical slags.

Most slags show only a gentle increase of $\ln \eta_{1900\text{ K}}$ and activation energy term ($B_A/1000$) when Q increases from 0 to 2, whereas, with values in the 3–4 range, glasses and molten minerals display exponential increases in both parameters with increasing Q .

5.2 Electrical Conductivity and Resistivity

Transport of electricity represents the movement of charges in response to the application of an electric field. The electrical resistivity is the reciprocal of the conductivity ($R = 1/\kappa$) and is a measure of the resistance of the silicate to the transport of these charges. Electrical conduction occurs by two different mechanisms in oxide melts in general and in molten slags in particular (Chapter 4.2):

$$\kappa_{\text{total}} = \kappa_{\text{ion}} + \kappa_{\text{elec}}. \quad (9)$$

The first mechanism is *ionic conduction*, which is usually predominant and is given by

$$\kappa_{\text{ion}} = F \sum c_i z_i n_i, \quad (10)$$

where F is Faraday constant and c_i , z_i , and n_i are the concentration, charge, and mobility of ion i , respectively. The transported species are usually cations since silicate anions tend to be large and sluggish and, thus, less mobile. At high temperatures, the principal factors increasing the ionic conductivity are (i) lower degrees of polymerization (i.e. low Q), which is a measure of the resistance to the flow of cations, (ii) higher concentration of cations available for transport (NB: this concentration is $N X_{MxO}$, where N is the number available cations, whereas for $X_{Na_2O} = X_{CaO}$ there are twice as many Na^+ ions as Ca^{2+} ions), and (iii) decreasing cation sizes.

The second mechanism is *electronic conduction*, which occurs by electron hopping between M^{2+} and M^{3+} ions, where M represents a multivalent transition metal, e.g. Fe (Chapter 4.2). Both M^{2+} and M^{3+} are needed for electronic conduction and κ_{elec} is at a maximum when $X_{M2+} \approx X_{M3+}$ [13]. In slags, it is appreciable only for high concentrations of transition metal oxides (i.e. with more than 60 % FeO_x), which results in a sharp increase in the electronic transference number [13].

The silicate structure resists both viscous flow and the movement of cations when an electric field is applied. Hence, the temperature dependences of the electrical conductivity and resistivity can be expressed as Arrhenius relations at superliquidus temperatures:

$$\kappa(\Omega^{-1} \text{ cm}^{-1}) = A_{\kappa} \exp\left(\frac{-B_{\kappa}}{T}\right), \quad (11)$$

$$R(\Omega \text{ cm}) = A_R \exp\left(\frac{B_R}{T}\right). \quad (12)$$

Alternatively, a VFT-like equation has to be used for supercooled liquids:

$$R(\Omega \text{ cm}) = A_{VR} \exp\left[\frac{B_{VR}}{(T - T_o)}\right]. \quad (13)$$

Values of $\ln R_{1900\text{ K}}$ and B_R , when plotted against Q for silicates and aluminosilicates (Figure 7), indicate that:

- i) Both parameters increase with increasing polymerization.
- ii) There is a gap between $MO-SiO_2$ and M_2O-SiO_2 curves, which is assigned to the difference in the available cations (N).
- iii) The scatter around the curves is not random since both $\ln R_{1900\text{ K}}$ and B_R values increase with increasing cation size.
- iv) Values of $\ln R_{1900\text{ K}}$ for aluminosilicates are lower than for silicates.
- v) Values of the activation energy term, B_R , are higher for aluminosilicates than for silicates.

Substitution of Al^{3+} for Si^{4+} in the structure results in:

- a) Simultaneous increases in the magnitude of Q and decreases in the number of available cations (N , because cations are needed for charge balancing) causing increases in both $\ln R_{1900\text{ K}}$ and B_R .
- b) A relative decrease in the resistance to viscous flow (Figure 6), cf. that for silicates since both $\ln \eta_{1900\text{ K}}$ and $B_{A\eta}$ are reduced.

The latter effect is more important for $\ln R_{1900\text{ K}}$, whereas the effect of Q and N is dominant for B_R (Figure 7c and d).

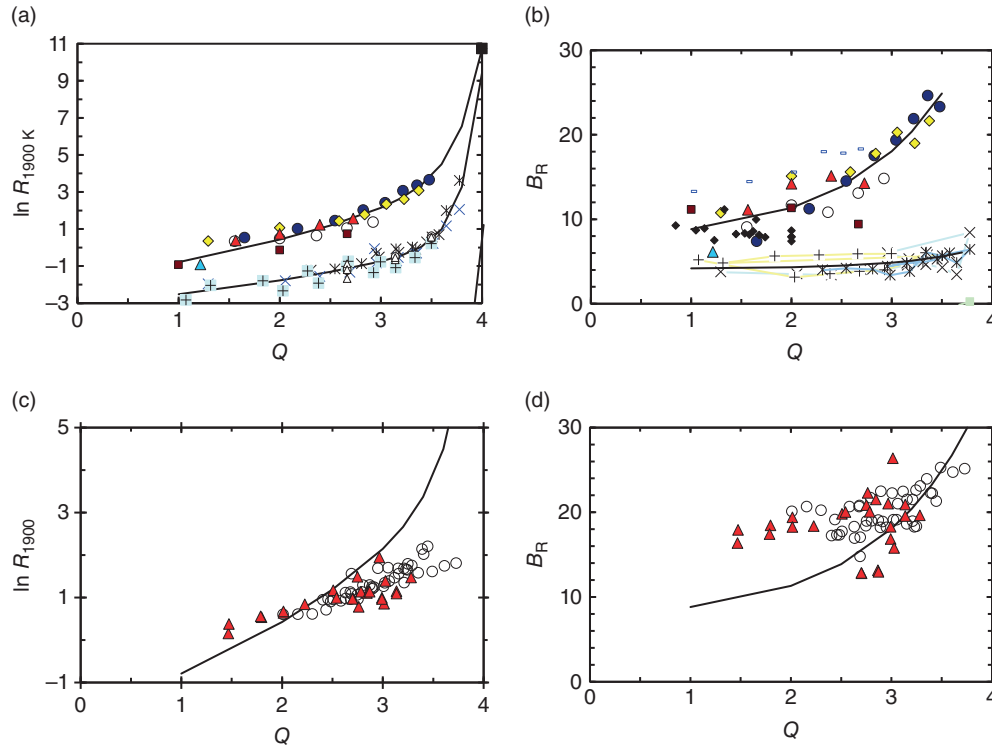


Figure 7 Effect of the polymerization parameter Q on the electrical resistivity of silicate (points) and aluminosilicate (curves) melts. (a) and (b) $\ln R_{1900\text{ K}}$ and activation energy B_R for silicates; + = LS; x = NS; * = KS; o = CS; ▲ = MS; ◇ = SrS; * = BS; ▲ = FS; ■ = MnS; ◆ = MFS. (c) and (d) $\ln R_{1900\text{ K}}$ and B_R for aluminosilicates [14].

As shown by Figure 7a and b, values of both $\ln R_{1900\text{ K}}$ and B_R depend less on Q for metallurgical slags ($Q = 0-2$) than for molten minerals and glasses ($Q = 3-4$).

5.3 Diffusion Coefficients (D)

Diffusion is a process whereby ions or atoms move through the sample by making a series of jumps from one vacant site to another. Diffusion takes place in the direction from a region of (high $\rightarrow$ low) concentration of the diffusing species. There are several types of diffusion, namely, self, tracer, impurity, and chemical (Chapters 4.3 and 4.4).

In addition, interdiffusion occurs when two or more species are involved, e.g. a cation and a large sluggish anion (Chapter 4.4). The anion moves more slowly than the cation, which results in the formation of an electric field that retards the cation and accelerates the anion movements.

Measurements of the diffusion coefficient (D) in liquid slags are prone to uncertainty because of the difficulty of eradicating convection in experiments. The diffusion coefficient is the equivalent to the electrical conductivity and the fluidity (i.e. reciprocal of viscosity). The experimental values of $\ln D$ tend to increase with:

- Decreasing degree of polymerization (Q) of the slag since silicate species resist the movement of ions.
- Decreasing size of the diffusing species ($\ln D$ values for, $\text{Li} \approx \text{Na} > \text{K} > \text{Rb} > \text{Cs}$).
- Increasing number of cations available for diffusion (N , which is related to $[2/Z]$ where Z is the valence of the ion).
- Increasing temperature (the temperature dependence for the liquid can be expressed as an Arrhenius relation, $D \text{ (m}^2 \text{ s}^{-1}) = A_D \exp(-B_D/T)$, and by a VFT relation for the supercooled liquid, $D \text{ (m}^2 \text{ s}^{-1}) = A_D \exp[-B_D/(T - T_0)]$).

Although the $\ln D$ values for geological melts are in the hierarchy $\text{Li}^+ \approx \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, the effect is less marked for M^{2+} cations ($\text{Ba}^{2+} \approx \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$). It has been proposed that there are two factors affecting the diffusion process in geological melts [15], namely:

- The detachment of the diffusing ion (i.e. through the breaking of the existing M–O bond).
- Its subsequent movement through the melt.

The overall diffusion coefficient will be determined by the slower of these two steps. In the case of M^+ ions, the M–O bonds are weak (z/r^2 is low), so detachment

is relatively easy, and thus D is determined by the movement of the M^+ ions through the silicate network (hence $Li^+ \approx Na^+ > K^+ > Rb^+ > Cs^+$) [16]. However, for the M^{2+} cations, the $M-O$ bond strength (related to z/r^2) is high, so detachment of M^{2+} ions is the slow step, and, thus, diffusion will increase as z/r^2 decreases (i.e. $Ba^{2+} \approx Sr^{2+} > Ca^{2+} > Mg^{2+}$). However, the hierarchy is also affected by the degree of polymerization (i.e. Q) since the amount of free space in the melt increases with increasing Q values. Thus for high- Q melts (e.g. molten minerals), there is plenty of space, and cation detachment is the controlling factor, whereas, in lower- Q melts (e.g. metallurgical slags), there is little space, and D is determined by cation size [16]. Metallurgical slags in general have low Q values and higher concentrations of M^{2+} than of M^+ ions. Application of the above theory to slags is a little confusing since (i) a low Q would mean D increases with decreasing cation size but (ii) the high M^{2+} concentration would indicate D increases with increasing cation size. More work is needed to clarify this point.

5.4 Thermal Conductivity (K)

Many silicates are considered to be *semitransparent* media through which heat is transferred by several mechanisms (Chapter 4.5), namely, (i) *phonon* or *lattice conduction*, (ii) *convection*, and (iii) *radiation conduction* (k_R , a mechanism that involves absorption of IR radiation and reemission). This complex situation poses severe measurement problems. One can minimize convection by using transient techniques such as the laser pulse (LP) and transient hot wire (THW) methods. However, the measured thermal conductivity (k_{eff}) for silicates may contain a k_R contribution of unknown magnitude. For an *optically thick sample* (defined as $\alpha*d > 3$ where $\alpha*$ = absorption coefficient and d = thickness of sample), k_R can be calculated ($k_R = 16\sigma n^2 T^3 / 3\alpha*$ where n is the

refractive index and σ the Stefan–Boltzmann constant); contributions from k_R rise sharply with increasing temperature owing to the T^3 dependence.

There is some uncertainty in measured thermal conductivity values [12] since:

- i) At the present time, there are large differences between the values obtained with the laser pulse (k_{LP}) and transient hot wire (k_{THW}) methods for temperatures higher than 1000 K (Figure 8); reported values for liquid slags of similar composition indicate $k_{LP} \approx 5 k_{THW}$. At this time no values of k can be recommended for slags above 1000 K.
- ii) One reduces contributions to radiation conduction (k_R) by (i) adding transition metal oxides (e.g. FeO, NiO), which increase the absorption coefficient of solid and liquid slags, and (ii) by promoting crystallization in solid slags since crystals, grain boundaries, and pores scatter IR radiation.

The temperature dependences of the thermal conductivities obtained with the LP and THW methods are similar below 1000 K but diverge markedly at higher temperatures (Figure 8a). At a certain point (denoted the critical temperature, $T_{crit} \approx 1000$ K), k_{THW} values drop sharply with increasing temperature, whereas k_{LP} values exhibit a gentle rise with increasing temperature up to T_{liq} , before showing a small decrease for the liquid.

This critical temperature occurs for k_{THW} values at the temperature where the viscosity attains a value of 10^6 dPa s, i.e. midway between the *softening temperature* (where the sample can no longer support its own weight) and the *flow point* (Chapter 1.1, [12, 16]). Furthermore, measurements of k_{THW} indicate that values of k_{298} increase with both increasing polymerization (Q) and increasing cation field strength (z/r^2). These findings are consistent with the view that the magnitude of the thermal conductivity (k_{THW}) of the solid is associated with the *rigidity* of the silicate network.

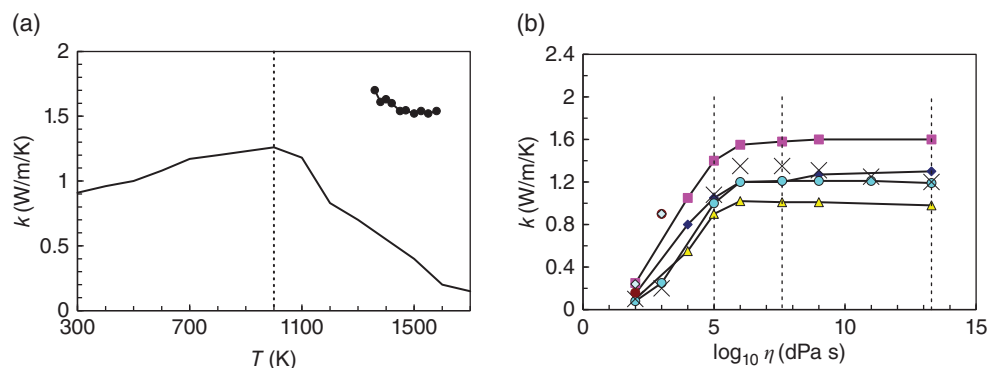


Figure 8 Thermal conductivity of $Na_2O-CaO-SiO_2$ slags of similar composition. (a) As a function of temperature; curve = k_{THW} ; o = k_{LP} . (b) As a function of $\log_{10}$ viscosity for four different slags; dotted lines (from left) T_{flow} ; T_{soft} ; T_{liq} .

6 Thermodynamic Properties

6.1 Thermal Expansion Coefficient

Referring to Chapter 3.5 for details, we just remind the reader that the coefficient of volume thermal expansion is given by $\alpha_V = (V_T - V_{298})/[V_{298} (T - 298)]$ where V is the molar volume.

The values of α_V for liquid silicates [9] decrease with:

- i) Increasing polymerization (i.e. Q).
- ii) Increasing field strength (z/r^2) of the cation.

The above factors also affect the thermal expansion of the solid. Values of α_l and α_V for both glassy and crystalline phases are similar from 298 K to T_g , but the transition from glass to supercooled liquid is accompanied by a large increase in α ($\alpha > T_g \approx 3 \alpha < T_g$). In contrast, α values for the crystalline phase maintain a smooth relation with increasing temperature.

6.2 Density (ρ) and Molar Volume (V)

The density (ρ) and molar volume (V) are linked via

$$\rho = \frac{M}{V}, \quad (14)$$

where M is the molecular weight of the slag and the effect of temperature on V is given by

$$V_T = V_{298} [(1 + \alpha (T - 298))]^3. \quad (15)$$

The molar volume of a slag is slightly affected by the degree of polymerization. Reasonable estimates of the molar volumes of liquid slags can be calculated from partial molar volumes (Eq. 16) for the various slag constituents, denoted 1, 2, and 3, but a plot of $(XV)_{\text{SiO}_2} - X_{\text{SiO}_2}$ exhibits a negative departure from linearity implying compaction in the structure. Thus polymerization results in reduction of the molar volume (or increase in density). The effect of Al_2O_3 on the molar volume is the reverse of that for SiO_2 :

$$V = \sum (XV)_1 + (XV)_2 + (XV)_3 + \dots \quad (16)$$

Crystalline phases have higher densities than glassy slags. Crystallization of a glassy slag results in some shrinkages causing porosity in the slag. There is an increase in molar volume (ΔV^{fus}) when crystalline slags melt, but values of ΔV^{fus} for the supercooled liquid are much lower because of the expansion associated with the enhanced α values above the glass transition.

6.3 Thermodynamics and Liquidus Temperature

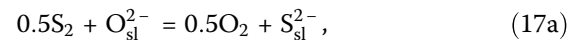
Thermodynamic properties are affected by the field strength (z/r^2) of the cations present:

- i) *Phase diagrams* for MO-SiO_2 systems exhibit miscibility gaps at high SiO_2 contents, the width of the gap increasing with increasing field strength of the cation (z/r^2), i.e. $\text{Mg} > \text{Ca} > \text{Sr}$ (Chapter 5.2).
- ii) The *liquidus temperatures* (T_{liq}) of $\text{M}_2\text{O-SiO}_2$ and MO-SiO_2 systems tend to decrease with decreasing field strength of the cation.
- iii) The *activity coefficients* of SiO_2 ($f_{\text{SiO}_2}^*$) in $\text{M}_2\text{O-SiO}_2$ and MO-SiO_2 systems increase as the field strength of the cation decreases (i.e. in the hierarchy of f^* , $\text{K}_2\text{O} > \text{Na}_2\text{O} > \text{Li}_2\text{O} > \text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$). In meta-aluminous aluminosilicates (i.e. $X_{\text{Al}_2\text{O}_3} = X_{\Sigma\text{M}_x\text{O}}$), the order changes since $f_{\text{SiO}_2}^*$ then increases as the field strength of the charge-compensating cations (i.e. in the order $(\text{Ca} > \text{Na} > \text{K})$ and with decreasing $2\text{Al}/(2\text{Al} + \text{Si})$ ratios [8, 9].
- iv) Values of the *enthalpy of solution* of meta-aluminous aluminosilicates in lead borate become more negative (i.e. more thermodynamically stable) as (z/r^2) for the cations (doing the charge balancing) decreases (i.e. in the hierarchy $\text{K} > \text{Na} > \text{Li} \approx \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$) [17].
- v) The *entropy of fusion* (ΔS^{fus}) for crystalline phases increases with (i) decreasing SiO_2 content and (ii) increasing field strength (z/r^2) of the cation [8, 9].
- vi) The *heat capacity* (C_p) and *enthalpy* ($H_T - H_{298}$) for crystals can be estimated in most cases to $\pm 2\%$ from composition-independent partial molar quantities; routines are available to estimate C_p and ($H_T - H_{298}$) for the supercooled liquids [9].

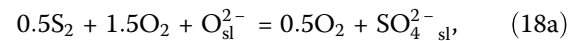
6.4 Sulfur and Phosphorus Capacities

Industrially, considerable effort is devoted to minimizing sulfur and phosphorus levels in molten metals because of the aforementioned deleterious effects of these elements. The concepts of S and P capacities (denoted C_S and C_P) have been defined to characterize the ability of a specific slag to withdraw these elements from the molten metal. These capacities are thus directly related to the partition coefficients, which for sulfur is, for instance, $L_S = [(\% \text{S})_{\text{sl}} / (\% \text{S})_{\text{m}}]$. The complication here is that the speciation of S and P must be taken into account when reactions between the molten metal and slag are considered and their equilibrium constants evaluated.

In the slag, sulfur coexists as sulfide and sulfates so that one has [18, 19]



$$K_1 = \left(\frac{a_{\text{S}}^{2-}}{a_{\text{O}}^{2-}} \right) \left(\frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right)^{0.5}, \quad (17b)$$



$$K_2 = \left(\frac{a_{\text{SO}_4}^{2-}}{a_{\text{O}}^{2-}} \right) \left(\frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right)^{0.5} \quad (18b)$$

Because the oxygen activity a_{O}^{2-} is high, however, in a first approximation, the low sulfur activity can be assumed to be constant, $a_{\text{O}}^{2-} = \gamma_{\text{S}}$, so the sulfur and sulfide capacities (C_{S}) simplify to [18]

$$C_{\text{S}} = \text{wt } \% \text{S} \left(\frac{p_{\text{O}_2}}{p_{\text{S}_2}} \right)^{0.5}, \quad (19)$$

$$C_{\text{SO}_4}^{2-} = \frac{\text{wt } \% \text{SO}_4^{3-}}{\left\{ (p_{\text{O}_2})^{1.5} (p_{\text{S}_2}) \right\}^{0.5}}. \quad (20)$$

Likewise [20], the analogous reactions and capacities for phosphide and phosphate capacities (C_{P}^{3-} and $C_{\text{PO}_4}^{3-}$) are given by

$$0.5\text{P}_2 + 1.5\text{O}_{\text{sl}}^{2-} = 0.75\text{O}_2 + \text{P}_{\text{sl}}^{3-}, \quad (21a)$$

$$C_{\text{P}}^{3-} = \frac{\text{wt } \% \text{P}^{3-} p_{\text{O}_2}^{0.75}}{p_{\text{P}_2}^{0.5}}, \quad (21b)$$

$$0.5\text{P}_2 + 1.5\text{O}_{\text{sl}}^{2-} + 1.25\text{O}_2 = \text{PO}_4^{3-}{}_{\text{sl}}, \quad (22a)$$

$$C_{\text{PO}_4}^{3-} = \frac{\text{wt } \% \text{PO}_4^{3-}}{(p_{\text{O}_2}^{1.25} p_{\text{P}_2}^{0.5})}. \quad (22b)$$

In practice, high S and P capacities thus are achieved with high-basicity slags.

6.5 Surface Tension (γ) and Interfacial Tension (γ_{msl})

Surface and interfacial tensions are not *bulk* properties because they are affected by *surfactants*, which tend to occupy preferentially the surface layers of the sample; typical ones are *soluble* S and O in the metal phase and B_2O_3 , K_2O , CaF_2 in silicates. The temperature derivative $d\gamma/dT$ tends to switch gradually from a negative to a positive value with increasing SiO_2 content; the crossover point is near $X_{\text{SiO}_2} > 0.5$. In metal processing, the interfacial tension (γ_{msl}) owes its great importance to the fact that it is a major factor in slag/metal kinetics and in slag entrapment. It can be calculated from

$$(\gamma_{\text{msl}}) = (\gamma_{\text{m}}) + (\gamma_{\text{sl}}) - 2\phi(\gamma_{\text{m}} \gamma_{\text{sl}})^{0.5}, \quad (23)$$

where the interaction coefficient (ϕ) increases with increasing Gibbs energy of formation per mole O for the oxides present. Because surface tension tends to be three or four times higher for the metal phase than for silicate melts, it is largely controlled by the former phase and hence is sensitive to the *soluble* O and S contents in the metal.

6.6 Comparison of Property Values for Metallurgical and Coal Slags and Molten Minerals

Property values for various slags are compared with those for minerals in Table 2. It can be seen that the viscosity increases with increasing degree of polymerization (Q). A similar comparison of the activation energy terms (B_{A}) would show an identical trend. The principal differences between the property values of glasses and minerals and those of metallurgical slags are due to the fact that the latter have a loose structure compared with the 3-D framework of minerals.

7 Perspectives

In the past, measurements of physical properties for slags have proved useful in understanding the mechanisms causing problems in process control and product quality. That remains the case, but a new demand for slag property data is likely to emerge in the future. Over the last 30 years, mathematical modeling of processes has improved to the point that they can now give insight into the mechanisms responsible for process problems. A good example is the model of the continuous casting of steel (Figure 3), which couples fluid flow, heat transfer, and the solidification of the steel shell [19, 20]. This model has not only correctly predicted heat fluxes and the consumption of slag but also revealed the mechanisms underlying defect formation (e.g. slag entrapment) (Figure 2) and the formation of oscillation marks [20]. The model actually allows one to *see into the mold* even at a very high temperature of 1900 K.

Mathematical modeling of processes will prove an ever-more important tool in improving process control and product quality in the future. However, these models need good, reliable property values for both slag and metal phases as input data (cf. Chapter 1.7 for analogous models in glassmaking). Physical property measurements are both time consuming and costly. There is a vast range of slag compositions used in metallurgical processing, and compositions tend to vary on a daily basis. Consequently, it is unrealistic to carry out property measurements on all slags. Thus, it is necessary to develop mathematical models to calculate reliable property values from slag chemical composition data (which is available on a routine basis). This will be a major challenge for the future and will require the model to describe not only the effect of polymerization but also the various cation effects, and this, in turn, will require a reliable description of the slag structure.

A final point should be noted. The continuous drive for improved process efficiency has caused the recycling of slag wastes (e.g. in cements; cf. Chapter 9.9) and energy capture from slags to become very active areas of research in recent years.

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7.5

Water Glass

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1 Introduction

By water glass one designates not only alkali-rich silicate glasses but also the liquid phases obtained either when these glasses are dissolved into water or when a silica phase is dissolved in alkaline lyes. They are also called “soluble silicates.” Water glass has in fact a long history as it was first mentioned by the Flemish chemist and physician Joan Baptista van Helmont who reported in 1648 in his *Ortus medicinae* [1] that “if one melts a fine powder of glass with a large amount of alkali and exposes it in a humid place, one will presently find that all the glass dissolves into a water” (see Chapter 10.11). But a long-standing practical interest in this material was raised much later in the 1820s when the Bavarian chemist and mineralogist Johann Nepomuk Fuchs (1774–1856) described applications of materials he termed himself *water glasses* such as “protectant against the rapid propagation of fire in theaters, as binder and paint films” [2]. His potassium silicate glasses contained more silica than van Helmont’s and thus had the interest of being stable against moist atmospheres but still soluble in water.

To optimize many more practical applications, the chemical composition of water glass has since then been varied not only through changes in the nature and concentration of the alkali cation but also through the incorporation of ammonium ions. As a result, this silicate family has become one of the most important inorganic chemicals, being added to detergents, cements, paints, adhesives, and binders, serving in water treatment and mineral ore flotation, or used as a starting product in the fabrication of ceramics or of specialty minerals such

as zeolites. Water glass provides concentrated, reactive silica in a liquid phase with a buffered alkalinity ensured by the weakly bonded alkalis. Hence, it has the great advantage of offering the versatility of silicate materials in the context of aqueous chemistry.

The composition of water glass is most simply characterized by the $\text{SiO}_2/\text{M}_2\text{O}$ ratio ($\text{M} = \text{Li}, \text{Na}, \text{K}$) on either a mol (R_m) or a weight (R_w) basis. (Note that $R_m = R_w \cdot F_M$, where the F factors are the ratios of the molar masses of the relevant alkali oxide and silica, namely, $F_{\text{Na}} = 1.032$, $F_{\text{K}} = 1.566$, and $F_{\text{Li}} = 0.497$). In 1998 the world production was estimated to lie between 3×10^6 and 4×10^6 tons, the majority in the form of sodium water glass. More recent data for 2010 claim the production of soluble silicates with a content of 740 000 tons of SiO_2 in Western Europe alone.

In this chapter we will thus review the production, structure, basic physical and chemical properties, and uses of these basic materials.

As a complement, we refer the reader to a review on older literature by Vail [3] and to more recent papers by Iler [4] and Falcone [5]. Vail covered the whole range from science via technology to application available at his time, Iler treated soluble silicates in his outstanding book on silica chemistry from a more fundamental side, and Falcone took up new developments with a focus on structure. As for production processes, additional basic information can be found in handbooks on technical chemistry (e.g. [5]).

2 Fabrication of Water Glass

2.1 Process I: Glass Synthesis with Subsequent Dissolution in Water

The most important fabrication process of liquid water glasses is melting of raw materials to produce alkali silicate glasses, which are subsequently dissolved in water.

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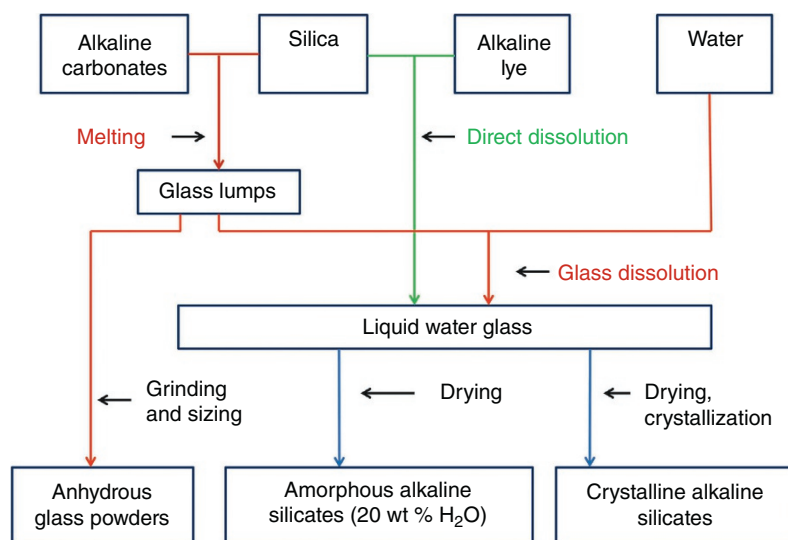


Figure 1 Process scheme for the productions of water glass and related materials.

The majority of the sodium water glasses and nearly all potassium water glasses are made by this process. As a matter of fact, the chemical durability of alkali silicate glasses with the same stoichiometry increases so much in the order $K \ll Na \ll Li$ [6] that lithium water glasses cannot be prepared by this process. In addition, Li-rich silicates such as lithium metasilicate (Li_2SiO_3) are poor glass formers, which also hampers dissolution because, for a given composition, the solubility in water is higher for the glass phase than for its crystalline counterparts.

The main steps of the process are sketched in Figure 1. Silica, alkali carbonates (e.g. Na_2CO_3 and K_2CO_3), alkaline brines ($LiOH$, $NaOH$, KOH), and water are used as raw materials. With silica having several polymorphs of economic interest, the very common α -quartz form (also known as low quartz) is the usual source for both the melting process and hydrothermal dissolution in alkaline lyes. Synthesis of sodium or potassium silicate glasses requires fast and total dissolution of quartz, which is achieved with melting temperatures between 1100 and 1400 °C [7]. The alkali oxides act as flux for silica. In most cases continuously operating melting tanks with regenerative heat recovery systems are used, but their lifetime is limited because high-alkali melts, the alkaline gas components evaporating from the melt into waste gases, and fine dusts are all strongly corrosive. When melting is completed, the fluid melt is often poured on metallic chain belts with molds and cooled rapidly to glass cullets or lumps. Typical lumps have a cross section of about $8 \times 8 \text{ cm}^2$ and a thickness of 3 cm. For some applications the glass lumps are ground, sieved, and screened in a dry atmosphere to yield anhydrous glass powders.

Thanks to their low chemical durability, alkali silicate glasses in the form of lumps or cullet rapidly dissolve in water to yield highly concentrated liquid water glasses.

In 2000 about 70% of liquid water glasses in Western Europe were produced with this process. Dissolution is performed as a batch process at temperatures up to 170 °C [7]. Rotating autoclaves or standing digesters with stirring or circulating liquid phase suitable for high pressures are applied. Above 100 °C the dissolving units have to oppose high water vapor pressure and are often heated with steam [7].

Because the melting tanks and dissolver units are inevitably corroded by the glass, they contaminate it with impurities that add up to those present in the raw materials or come from the fossil fuels burned in the process. These impurities influence the properties and applicability of the liquid water glasses. Highly charged cations are problematic because they can trigger the precipitation of silicate crystals. A filtering step with a cutoff in the high nm range (e.g. 450 nm) thus usually increases purity. For commercial liquid water glasses, typical impurities are CaO (not detected up to 150 ppm), MgO (n.d. to 40 ppm), Al_2O_3 (80–1700 ppm), Fe_2O_3 (20–120 ppm), and TiO_2 (60–200 ppm). As described by the patent literature, higher purities, e.g. for applications in electronics, can be achieved by filtration in the lower nanometer range, ion exchange, and electrochemical methods.

One can then adjust the composition of the water glass by dilution with or evaporation of water, by ion exchange to remove alkalis, or by mixing liquid water glass with alkaline lyes. If needed, one can also increase the R_m ratio of the product by dispersing silica materials with high specific surface area in liquid water glass or by combining colloidal silica with glass lumps upon dissolution.

The dissolution process itself depends on glass composition, temperature, pH, and concentration of the liquid water glass. It begins with an exchange of alkalis for protons, which causes the pH to increase to values higher

than 9. Under these pH conditions, a steady state is established for network dissolution and ion exchange. At higher temperatures the silicate network disintegrates directly into colloidal silica [8].

2.2 Process II: Dissolution of Silica Phases in Alkaline Lyes

The second process used to fabricate water glass bypasses glass fabrication to rely instead on dissolution of silica phases in alkaline lyes. A variety of silica phases such as quartz, cristobalite, tridymite, calcined rice husk, and vitreous or pyrogenic silica can dissolve to a certain degree. Temperatures between 160 and 250 °C in pressure-tight dissolution units or autoclaves are applied. By dissolving quartz sand in NaOH lyes one can reach R_m values up to 2.7 [7]. Cryptocrystalline and vitreous or colloidal silica, which have a lower chemical durability than α -quartz, can be used to enhance the rate of the dissolution process and to increase the R_m value of the products.

In the case of potassium water glass, the R_m ratios attainable by hydrothermal dissolution are too low for technical applications. One reason is the crystallization of KHSi_2O_5 under hydrothermal conditions as reported already by Morey and Fenner [9].

Lithium water glasses are prepared by dissolution of silica phases with a high specific surface area in LiOH lyes [7]. To prepare ammonium water glasses [10], aqueous ammonium hydroxide solutions are first mixed with dilute sodium water glass, and then sodium is extracted by ion exchange. If ammonia is replaced in that process by amines like monoethanolamine, one obtains quaternary ammonium silicates. Quaternary ammonium is an organic cation with a +1 charge consisting of nitrogen bonded covalently to four alkyl or aryl groups.

2.3 Production of Crystalline Sodium Silicates

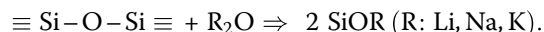
Anhydrous sodium metasilicate (Na_2SiO_3) can be produced as a crystalline material through reaction of silica with sodium carbonate from 850 °C, the melting point of soda, to temperatures slightly below its own melting point at 1018 °C or through crystallization of a quite corrosive glassmelt. Alternatively, the anhydrous sodium metasilicate can be prepared through drying of sodium water glass. Sodium silicate hydrates are obtained by direct hydration of the anhydrous metasilicate or by drying sodium water glass at lower temperatures. Layered sodium silicates are produced by spray drying or by crystallization from seeded (with the desired crystalline product) concentrated liquid water glasses at temperatures above 70 °C. In many cases a heat treatment at temperatures of up to 800 °C is necessary to obtain the desired

modifications. The reaction products are ground, sieved, and screened after drying [11].

3 Materials and Chemical Stability and Structure

3.1 Alkali Silicate Glasses

Alkali silicate glasses contain one network former and one network modifier (see Chapter 2.4). Each sodium atom introduced into the structure creates one nonbridging oxygen, which decreases the polymerization degree of the structure:



Important consequences of this network depolymerization are lower liquidus and melting temperatures and lower chemical durability of the glasses.

The structure of alkali silicate glasses has been investigated with various methods like NMR spectroscopy, molecular dynamics simulations, or scattering (Section II). Some investigations indicate the formation of nanoscopic clusters, e.g. sodium-rich channels and silica-rich islands (see Chapter 2.5). Such a microstructure provides paths for the intrusion of molecular water or protons and explains the direct disintegration of the glass into colloids described in [8].

At high silica content this nanoscopic segregation gives way to metastable phase separation with a miscibility gap that increases in the order $\text{K} < \text{Na} < \text{Li}$ (Chapter 5.2). For sodium silicates, the sodium-rich branch of the solvus is found at 20 mol % Na_2O , which thus represents the lowest Na_2O content possible for sodium silicate glasses applicable for the production of liquid water glass.

3.2 $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$

Liquid sodium water glasses are the most common types. Standard products have R_m values of 2 ("alkaline" water glass") and 3.3 ("neutral water glass"), but the whole ranges are $R_m = 2-2.2$, 3.3-3.5, and 3.9-4.1, with SiO_2 content going up to 35 wt %. The compositions of some important materials are shown in Figure 2, whereas a few basic properties [12] are listed in Table 1 for compositions of practical interest. Phase equilibria have been investigated in the ternary system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ (e.g. [13]). At 200 °C a liquid water glass with 27.5 wt % SiO_2 and $R_m = 2.83$ is, for instance, in equilibrium with α -quartz, in agreement with the findings that liquid sodium water glasses with $R_m < 2.7$ can be produced by hydrothermal dissolution of low quartz. At higher temperatures, the solubility of silica decreases.

Crystalline sodium metasilicate hydrates of formula $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ with $n = 0, 5, 8$, and 9 are common [5].

Other crystalline materials are the so-called layered sodium silicates whose structure consists of layers of SiO_4 tetrahedra interconnected via sodium ions. One type of these layered sodium silicates comprises several modifications of the disilicate ($\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$). Especially the $\delta\text{-Na}_2\text{O} \cdot 2 \text{SiO}_2$ modification is used for ion exchange of alkalis against water hardeners like Mg^{2+} or Ca^{2+} . Other types of layered sodium silicates have higher R_m ratios. Some of them occur in natural salt lakes, e.g. magadiite ($\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot 11 \text{H}_2\text{O}$) or kenyaite ($\text{Na}_2\text{Si}_{22}\text{O}_{45} \cdot 10 \text{H}_2\text{O}$). Synthetic variants with comparable compositions are described in the patent literature for applications based on their intercalation abilities for surfactants in detergents.

3.3 $\text{K}_2\text{O}\text{--SiO}_2\text{--H}_2\text{O}$

The R_m ratio of commercial liquid potassium water glasses varies between 3.3 and 3.5 and 4.0–4.3, with SiO_2 contents reaching 25 wt %. The system $\text{K}_2\text{O}\text{--SiO}_2\text{--H}_2\text{O}$ was investigated by Morey and Fenner above 200°C [see ref. 9]. At

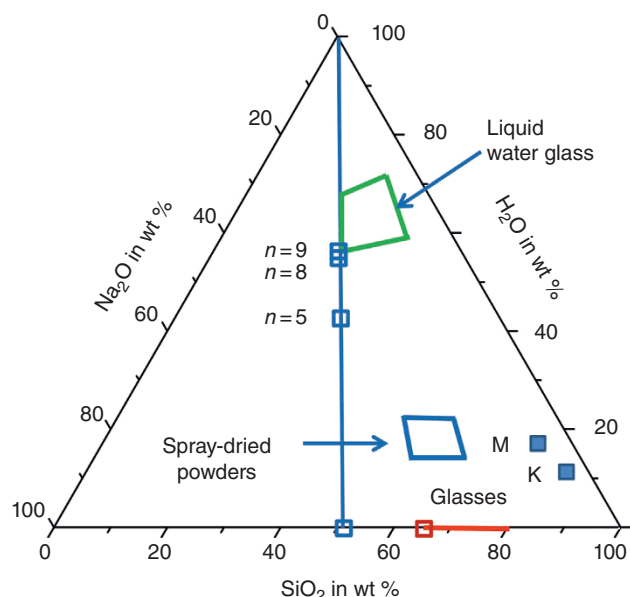


Figure 2 Ternary diagram $\text{Na}_2\text{O}\text{--SiO}_2\text{--H}_2\text{O}$; crystalline $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ with different values of n at the center; M, magadiite; K, kenyaite.

200°C , up to 24 wt % potassium silicate with $R_m = 2.0$ is dissolved in a liquid that is in equilibrium with potassium disilicate monohydrate ($\text{K}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$) and potassium tetrasilicate monohydrate ($\text{K}_2\text{O} \cdot 4 \text{SiO}_2 \cdot \text{H}_2\text{O}$ or KHSi_2O_5).

3.4 Other Types of Water Glass

Lithium-containing water glasses with R_m ratios between 3 and 9 and SiO_2 contents up to 20 wt % are produced by dissolution of ion-exchanged silica gels or colloidal silica in LiOH lyes [7]. Lithium cations probably stabilize larger amounts of silica colloids, thus allowing products to be made with higher R_m ratios combined with appreciably low viscosity.

Besides, ammonium-bearing water glasses have been introduced by Weldes [10]. Here defined as the molar $\text{SiO}_2/(\text{NH}_4)_2\text{O}$ ratios, R_m values of these materials range from 2 to 6 and SiO_2 contents from 6 to 12 wt %. Organic ammonium silicates or quaternary ammonium water glasses ($\text{A}_4\text{N} \cdot x\text{SiO}_2$, A: butyl, ethyl, etc.) have also been synthesized. Mixed alkali water glasses that contain more than one type of alkali are described in the literature, mainly for binder applications that require the higher chemical durability provided by adding lithium water glass.

3.5 Solubility of Silica at High pH

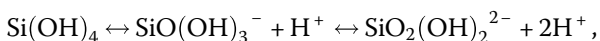
Sometimes molecular and colloidal solubilities are distinguished. Colloids are solid particles dispersed in a continuous medium with sizes comprised between 1 and 100 nm. Silicate molecules with more than 10 SiO_2 units have already diameters in the colloidal size range. Therefore, a distinction between large molecules (or macromolecules) and colloids is probably not significant. Nevertheless, molecules or colloids are treated separately here because they require different characterization techniques.

The older literature on the solubility of silica modifications was evaluated by Iler [4]. The solubility of silica depends on coexisting equilibrium phase, temperature, pressure, pH, and size of solid particles. Iler reported that the solubility of quartz is about 10 ppm under neutral conditions at room temperature. Other silica

Table 1 Composition and properties of liquid alkaline silicate water glasses [12].

R_m	SiO_2	Na_2O	K_2O	density ρ	Dynamic viscosity η	pH
	in wt %			in g/cm^3	in mPa s	
2.0	24.7	12.3		1.437	44.7	13.0
3.3	25.2	8.0		1.327	21.2	12.1
3.3	24.4		12.4	1.358	24.3	12.5
4.0	19.9		8.3	1.239	8.7	12.1

modifications may have higher solubilities. Their solubilities increase with temperature and pH. That of Si(OH)_4 reaches about 1000 ppm under hydrothermal conditions at 300 °C. The solubility of amorphous silica is higher than that of α -quartz. Si(OH)_4 is a weak acid which dissociates especially at basic pH:

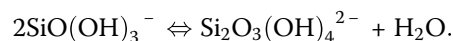


thereby deprotonating silanol groups and creating a negative charge. Iler [4] calculated thermodynamic equilibria between Si(OH)_4 , SiO(OH)_3^- , and $\text{SiO}_2(\text{OH})_2^{2-}$ at 25 °C. Above pH 9 the solubility of silica increases because of the pH-dependent formation of the silicic anions mentioned above. Iler restricted his calculations to pH values below 10.5. An extrapolation of his data to the higher pH range of liquid water glasses yields solubilities that are probably too large (Figure 3). More detailed information can be derived on solubility fields from the data of Falcone et al. [14] and Stumm and Morgan [15]: in domain A - (Figure 3, inset), alkali silicate solutions are unstable; in domain B, liquid water glasses containing "multimeric" silica are in contrast stable; and in domain C, alkali silicate solutions containing only monomeric silica species are found. Whereas multimeric silica comprises large molecules and colloidal silica, the thermodynamic calculations made by Iler considered only monomeric species. Because the line representing the total silica content of monomeric species in Figure 3 lies within domain B, it appears that the extrapolation toward higher pH values does not agree totally with experimental data.

3.6 Structure of Liquid Water Glass at a Molecular Scale

Liquid water glasses contain silicic acid molecules Si(OH)_4 and anionic silicic species. Investigations by Raman and infrared (IR) spectroscopy [14] confirm Iler's thermodynamic calculations and indicate that SiO(OH)_3^-

and $\text{SiO}_2(\text{OH})_2^{2-}$ are the main anions at basic pH values, whereas Si(OH)_4 prevails in the acidic region [4]. These anions and molecules reflect the tetrahedral structure typical of silicates and can be regarded as monomers building up larger units by condensation reactions of the following type:

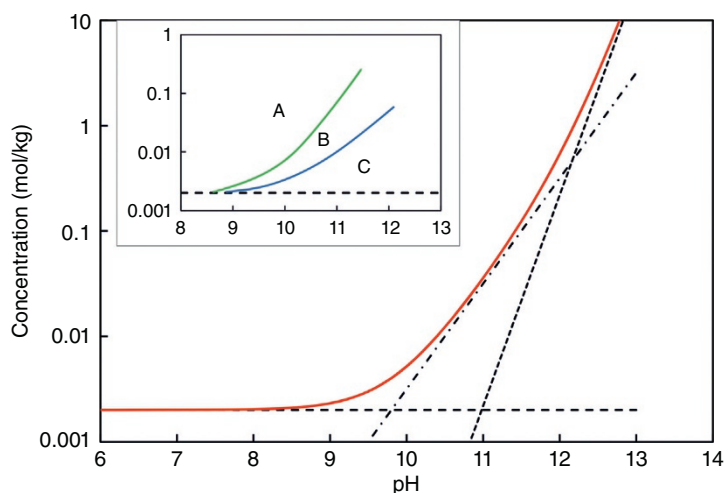


Theoretically, there is no limit to condensation, and also large molecules or colloids are formed by these reactions. The molecules can ionize in aqueous solutions. Charge compensation is then provided by cations such as H^+ or M^+ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{etc.}$).

One of the first methods to study the structure of oligomeric silicate anions was trimethylsilylation. Upon addition of trimethylsilane to the solution, the protons of OH groups are replaced by SiMe_3 ($\text{Me} : \text{CH}_3$), which inhibits further reactions of silanol groups and allows silicate anions to be separated by chromatography. Andersson et al. [16] identified in this way anions with up to eight silicon atoms. These investigations have been supplemented with ^{29}Si NMR spectroscopy. Different silicate anions with up to 12 silicon atoms have been detected in dilute water glasses enriched in ^{29}Si . Investigations on liquid water glasses with technical compositions allowed the Q^n speciation to be determined, where Q^n denotes silicon atoms connected via bridging oxygens to n other silicon atoms (Chapter 2.4). Bahlmann et al. [17] made quantitative ^{29}Si NMR measurements and showed that a sodium water glass with 30 wt % SiO_2 and $R_m = 3.4$ contains 0.6 % Q^0 , 4.7 % Q^1 , 29.8 % Q^2 , 50.3 % Q^3 , and 14.6 % Q^4 units, all Q^4 and part of Q^3 units building up colloidal silica at the surface of which the latter are present.

Additional information can be obtained by Raman and IR spectroscopy. Especially the spectral range from 800 to 1200 cm^{-1} can be investigated to identify and quantify silicate species in liquid water glasses. Falcone et al. [14]

Figure 3 Concentrations of silicate species in equilibrium with colloidal silica as a function of pH according to Iler [4]. Inset: stability fields of monomeric (C), oligomeric (B), and polymeric (A) liquid water glasses according to Falcone et al. [14] and Stumm and Morgan [15].



applied this means and showed that the concentration of monomeric silica stays constant during further polymerization that they induced by replacing sodium with tetramethylammonium.

3.7 Structure of Liquid Water Glass at a Colloidal Scale

Colloids in liquid water glasses are supposed to consist mainly of silica. Iler [18] argued that alkalis are necessary to stabilize the colloidal surface. The colloid stability depends on an electric double layer formed of negatively charged deprotonated silanol groups and positive sodium ions that are partially hydrated. He concluded that alkali concentration limits the surface area of colloids, which act like micelles in tenside solutions by “hiding” the silica that cannot be stabilized by charge-compensating alkali ions. One consequence is that liquid water glasses with higher R_m values but identical SiO_2 content have fewer and smaller colloids because of their higher alkaline content. Iler applied static light scattering and detected 10% monomers, 75% colloids with a diameter of about 1.8–1.9 nm, and 15% oligomers in concentrated liquid sodium water glass ($R_m = 3.2$). Newer investigations by dynamic light scattering [19] have shown the existence of particles exhibiting several maxima in their size distribution between 1 and 100 nm even in strongly dilute sodium water glasses. This is demonstrated in Figure 4 for a sodium water glass with $R_m = 2.2$, a composition supposed to be less liable to colloid formation than those with smaller sodium concentrations. The larger colloids probably formed by aggregation of smaller ones and are deformable since they can pass filters with pore sizes smaller than their particle size [12]. This study also showed that the applied synthesis routes – dissolution of glass with $R_m = 2.0$, dissolution of quartz ($R_m = 2.0$), and dissolution of a glass with $R_m = 3.3$ and subsequent mixing with NaOH lyes – yield concentrated liquid water

glasses that have almost the same structure at a molecular scale but present some differences in the particle size distribution of colloids.

Tognonvi et al. [20] combined ^{29}Si NMR spectroscopy and small-angle X-ray scattering to describe solvated silicate ions to conclude that the primary building unit in concentrated liquid water glasses with $R_m = 3.4$ is a neutral $\text{Si}_7\text{O}_{18}\text{H}_4\text{Na}_4$ complex with a size of 0.6–0.8 nm. This complex dissociates into silicate and sodium ions when water glass is diluted. The silicate ions then condensate to larger units containing two to eight of these complexes, a finding that is in agreement with colloid sizes between 0.8 and 2 nm, which have been found by light scattering.

The aforementioned surface stabilization depends on pH and alkali concentration. Changing these parameters may destabilize the colloids and lead to flocculation.

According to phase diagrams, most of liquid alkaline water glasses are not in thermodynamic equilibrium. On the other hand, as shown above, different synthesis routes yield nearly identical structural results on a molecular scale [12]. Hence, liquid water glasses should be in metastable equilibrium at the temperatures that are typical of dissolution processes. This equilibrium is characterized by ongoing hydrolysis and condensation reactions. To obtain a stable thermodynamic equilibrium, the precipitation of the crystalline equilibrium phase would be required. At ambient temperature, however, the kinetics of structural rearrangements by hydrolysis and condensation becomes too slow probably because the concentration of monomeric units decreases with temperature. Additionally steric barrier effects and stabilization of colloidal dispersions by an electrostatic double layer at their surface are more effective at lower temperatures because the kinetic energy of the colloids then is lower.

In summary, the structure of concentrated liquid water glasses can be described as complex colloidal suspensions

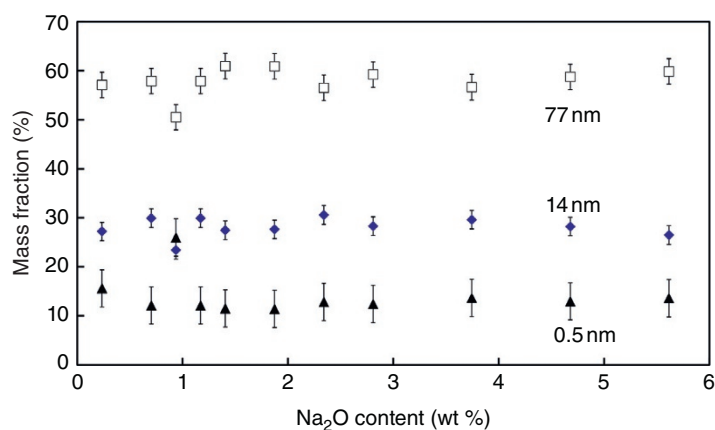


Figure 4 Mass content of colloidal size classes measured by dynamic light scattering [19] as a function of sodium oxide content for liquid sodium water glass with $R_m = 2.2$; water glass diluted by mixing with deionized water, measured within two hours after mixing; radius of colloids included in the figure.

in aqueous alkali silicate solutions. Since sols are colloidal suspensions, liquid water glasses can be also addressed as alkali silicate sols.

4 Properties of Water Glass

4.1 Refractive Index, pH, Density, and Viscosity

The refractive index, pH, density, and viscosity are basic properties that can be used for quick quality control [3, 12] (see Table 1 for standard materials). The refractive index and density are in a first approximation additive functions of composition in terms of the three main components M_2O , H_2O , and SiO_2 [3], but they vary slightly with impurity concentration and thermal history of the liquid water glasses from synthesis onward.

When measured against the sodium content of the solutions, the near constancy of the pH between 10 and 13 at high alkali concentration indicates that liquid water glasses act as a pH buffer (Figure 5), a property useful in many applications where liquid water glass provides an alkali reservoir under intermediate basic conditions. A look at the pH of concentrated solutions (Table 1) shows that the OH^- concentration and the overall Na content of the liquid water glass are not equal. A sodium water glass with $R_m = 3.3$ has a Na concentration of 1.9 mol/l. If all Na were acting as counterions for OH^- groups, a pH of 14.3 would result whereas the measured pH is 12.1. The majority of Na thus is adsorbed on negatively charged surface sites to stabilize colloidal silica.

Viscosity measurements of dilution series of liquid water glasses show a dependence typical for spherical particles [21]. Although dilute liquid sodium water glasses have a Newtonian viscosity, shear thickening has been observed at higher concentrations.

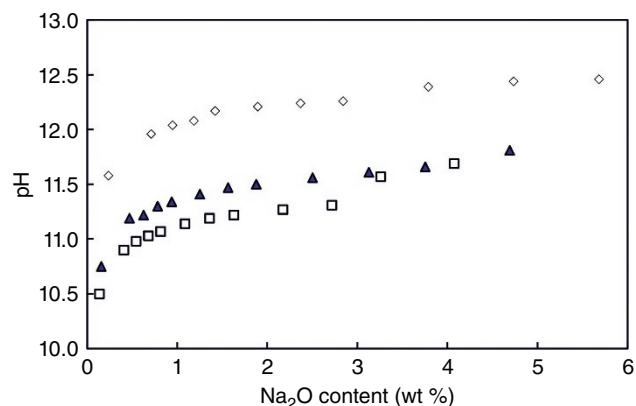


Figure 5 Effect of dilution with deionized water on the pH of sodium water glass; data from [19].

4.2 Chemical Reactivity

The chemical reactivity of water glasses depends on their composition and on thermal history, which influences the particle size distribution of the colloids. In reactions where they provide silicate ions or alkalinity, the depolymerization reactions of oligomeric and colloidal silica are of importance. The chemical reactivity can be characterized by the reaction of $Si(OH)_4$ with molybdic acid to the yellow silicomolybdate complex, where the optical absorption is a measure of the concentration of the silicomolybdate complex. Polymeric silica has to depolymerize first before it can react with the molybdic acid. Therefore, the kinetics of the silicomolybdate formation can be used to characterize the depolymerization kinetics. The literature on that topic was reviewed by Iler [4]. The polymerization takes place at room temperature within 10–30 minutes and is usually fast enough. The adsorption of multivalent metal ions on polymeric silica has been discussed by Falcone [5], who states that the absorption efficiency increases with polymerization degree.

5 Applications of Water Glass

An overview on uses of soluble silicates is given by Falcone [5]. Soluble silicates are “commodity chemicals” produced mainly as intermediate products. Half of them are applied for the synthesis of silicate materials; 40% are used as detergents, in the paper industry, and for soil stabilization; and 10% are used as additives to other products or as binders.

5.1 Liquid Water Glass and Amorphous Materials: Gels, Silica Sols, Precipitated Silica, and Dried Water Glasses

Liquid water glass is used as alkaline buffer, e.g. in the paper bleaching process with H_2O_2 as bleaching agent, as accelerator in concrete where it hardens the cement within 15 minutes, and as binder. Another application is the conservation of building stones, especially with potassium or lithium water glasses. When added to particle suspensions (ore, ceramic particles), liquid water glasses can interact with the surface of the particles and influences pH. These changes can be applied to foster filtration or flotation processes and to stabilize and liquefy ceramic suspensions.

Sodium water glasses are the common precursors for the preparation of silica materials. When neutralizing liquid water glasses with acids, the silicates polymerize [4, 5] to a sol of colloidal silica (basic pH 7–10, no salts present) or to more linear structures (pH < 7 or at slightly basic conditions with salt being present) forming a gel. Wet

gels can be used as templates for reactions or for crystallization processes. Dried gels are called xerogels and are powders with high specific surface areas and nanosized pores, which make them efficient desiccants or adsorbents. To produce aerogels, the wet gels have to be gently dried to avoid cracks caused by capillary forces, which one achieves by working under hypercritical conditions or by deactivating the silanol groups at the silica surface.

The term “colloidal silica sol” designates stable dispersions of amorphous silica colloids. One produces colloidal silica by careful neutralization of alkali silicate solutions with acids such as H_2SO_4 to pH values between 7 and 10 or by extracting alkalis with ion exchange – which also lowers the pH [4]. The final particle size ranges from 5 to 150 nm and depends on both the precipitation process (time, temperature, reactants) and the aftertreatment (temperature, colloid stabilization). The resulting sols are usually stabilized by alkalis or ammonia.

Precipitated silica is a nanoscale silica powder with a high surface area and an internal porosity that is obtained from colloidal silica sols, which are described above. The sols are washed and dried in drums or by spray drying. They are, for instance, applied to reinforce elastomers, e.g. as a substitute for carbon black in tires. The reinforcement is attributed to interactions via phase interfaces, and the high surface area of colloidal silica leads to larger effects. Precipitated silica is also used as additive in foodstuff in which it either prevents powders from caking or improves the flow characteristic of liquids. In some aspects it is comparable to pyrogenic silica, which can be made by flame hydrolysis of SiCl_4 .

The application of water glasses as fire-retarding materials was already mentioned by Fuchs [2]. If liquid water glasses are applied as coating or film, they dry to solid amorphous material containing residual water, which absorbs IR radiation and foams if heated to about 140°C . If a continuous layer of liquid water glass is carefully dried under controlled atmospheres on a flat surface, e.g. a window pane, it forms transparent amorphous solid sheets. Commercial types of these transparent materials contain organic additives (e.g. to prevent ice crystallization during cold weather) and are also used as transparent intumescent layers in fire-resistant glazings. Because dried potassium water glasses have lower water contents, sodium water glasses are the superior materials for this application.

Liquid water glasses can be spray-dried to yield alkali silicate powders with water contents of about 20 wt %. The powders dissolve very quickly in water and are used in detergents or in binders to supply reactive silica and alkalinity very fast.

5.2 Crystalline Materials: Zeolites and Crystalline Sodium Silicates

Liquid water glasses and mineralizers (e.g. sodium aluminate) can react under hydrothermal conditions to form zeolites. These framework aluminosilicates have holes filled with ions or molecules in their structure, which enable them to be used for ion exchange, absorption, or catalysis. Important products are water softeners and industrial catalysts.

Layered sodium silicates are applied as ion exchangers: their sodium ions exchange with metal cations. In the case of ion exchange with Mg^{2+} or Ca^{2+} , they act as water softeners or builders.

5.3 Binders

The solidification of water glass used as binder occurs via drying to a solid, reaction with atmospheric CO_2 , neutralization with an acid, or reaction with specific hardeners such as sodium or aluminum phosphates. Liquid water glasses as well as powder varieties (anhydrous or water containing alkali silicate materials) can be applied in binder formulations or as additive to other binders. The application for foundry sands is revived due to environmental reasons. New types of binders are alkali activated cements and geopolymers where the alkalinity of NaOH lyes or water glass accelerates the hydration reactions of aluminum silicates or of pozzolans. Potassium water glass is applied as binder in pigmented paints because it does not effloresce under ambient atmosphere [7]. Lithium water glasses are required when a higher chemical resistance of binders or paints or lower alkali contents is required. Quaternary ammonium containing water glasses can be used as binders [13] for higher temperatures since they contain no alkalis reacting as flux for acidic oxides.

6 Perspectives

Research and development on water glass concentrates on lowering both energy consumption and CO_2 output during production and the development of new and environmentally friendly products. On both counts, hydrothermal dissolution of silica has clear advantage. New applications like alkali activated binders, which may substitute at least partly ordinary Portland cements and introduce new features like higher temperature or chemical resistance, will also enhance the importance of water glass. On the scientific side, a better understanding of the structure of water glass with its balance between smaller

molecules and colloids and of the thermodynamics of the system will also be important for improving existing products and designing new ones.

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7.6

Borosilicate Glasses

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1 Introduction

Borosilicates have made a late showing in the four-millennia glass history. They appeared only in the nineteenth century when, with the burgeoning growth in optics and a concomitant need for better lenses, scientists like Michael Faraday (1791–1867), in England, and Ernst Abbe (1840–1905) and Otto Schott (1851–1935), in Germany, looked beyond the typical crown and flint glasses of their days. The old method of correcting optical aberration through multiple lenses with different optical properties was, for instance, cumbersome, expensive, and only marginally successful, especially with the growing demands from telescope and microscope technology. As Faraday explained in a series of lectures on his research to improve optical glasses [1], addition of boron oxide was a simple means to obtain more homogeneous glasses for better optical performance.

Abbe, who recognized this need, had the good fortune of engaging the mind of a young Otto Schott, who began to work on different glasses for these types of applications. In 1884, the Schott & Associates Glass Technology Laboratory in Jena began production of a series of new optical glasses containing boron oxide – the first commercial venture in which boron oxide was a significant component. Introduction of B_2O_3 did eventually solve the problem of chromatic aberration and led to a revolution in optical glass [2]. This event marked the first of a long series of commercial successes met by the new glass family, which was, for instance, quickly followed by the development of thermal shock-resistant glasses for lamps.

At the roots of this advancement was an unusual easiness to prepare homogeneous glasses and the possibility to obtain the very low coefficients of thermal expansion (CTE) needed to ensure resistance to thermal shocks caused by rapid changes in temperature. Hence, after a brief review of the main uses of borosilicate glasses, the main concern of this chapter will be to account in structural terms for such outstanding features. As established by pioneering work made by Weyl [3] and Abe [4] in the mid-twentieth century, the most important factor in this respect is the complex speciation of boron, which is either three- or fourfold coordinated with oxygen, as B(III) or B(IV) units, respectively, and varies with chemical composition, temperature, and pressure. Particular interest will thus be paid to these variations and also to the superstructural units associated with the different boron polyhedra. Emphasis will be placed on glasses in the sodium borosilicate ternary, which exhibits a large compositional region of glass formation and an extensive and well known immiscibility but also contains within it some of the most important commercial borosilicate glasses (Figure 1).

2 Borosilicate Applications

2.1 Early Products

Some of the first commercial borosilicate glass compositions offered by Schott & Associates Glass Technology Laboratory, later Jena Glass Works and now Schott AG, are listed in Table 1. The initial optical glass facilitated the development of microscopy in medicine and telescopic instruments for astronomy. After heat tolerance had been discovered by Schott in 1892, his *Jena Apparatus Glass*, which was in addition highly resistant to chemical attack, thus became widely adopted in

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chemistry labs. In 1893, Schott found a new borosilicate glass that was insensitive to sudden changes in temperature. Since this material was “practically indestructible for incandescent lamp cylinders,” it became a huge

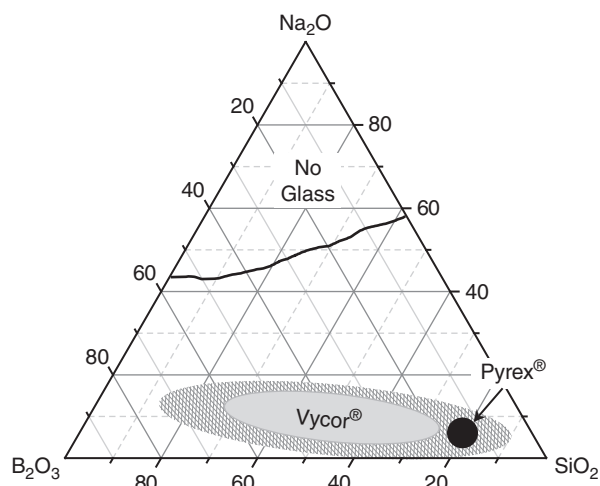


Figure 1 The $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{SiO}_2$ phase diagram, with estimated compositional limits of glass formation and large region of immiscibility (hatched area). Pyrex- and Vycor-related regions are denoted.

commercial success [5]. Prior to the development of this composition (Table 1), glasses used for this application had long been known for instability and loss of accuracy over time.

Shortly after Schott & Genossen commercialized borosilicate glasses, Corning Glass Works in the United States began to experiment with them, greatly facilitated by a “candid exchange of idea” between Jena and Corning [5]. Corning’s first product was for Fresnel-type lenses in railroad lanterns (high-temperature arc lamps), which solved a critical failure mechanism through thermal shock resistance. Soon after, a glass named Nonex (Corning nonexpansion glass) was introduced as a heat-resistant lantern-globe glass.

Borosilicate glasses, and perhaps the glass industry in general, were then significantly impacted by World War I, during which the United States and England were both at risk of losing critical supplies of high-quality optical glass made in Germany. This threat ultimately concerned a larger scientific community in that chemical- and heat-resistant laboratory glassware, made from a Schott & Genossen borosilicate glass composition, was also in short supply. By 1915, Corning had solved this particular issue and made a historical contribution to glass science by inventing and commercializing Pyrex [6],

Table 1 Approximate composition (wt %) of representative borosilicate glasses of commercial or historical importance.

	Thermometer glass 59 ^{III} (1889) ^a	Utensil glass 202 ^{III} (1892) ^a	Chimney glass 276 ^{III} (1895) ^a	Code 7740 Pyrex (1915) ^{b,c}	Corning Code 1737 ^b	NEG Code OA-2	Borofloat® 33 ^a	ISG ^d	E- Glass ^e
SiO ₂	79.75	73.72	75.71	80.6	58.4	55	81	56.2	54.5
B ₂ O ₃	7.53	6.2	15.27	12.6	8.49	7	13	17.4	6.6
Na ₂ O	7.13	6.62	4.08	4.2			4 ^f	12.1	1.0 ^f
MgO	0.06	5.48		0.05	16.4 ^g				0.6
CaO						24 ^h		5.0	22.1
ZnO		4.39				0.5			
Al ₂ O ₃	5.54	3.29		2.2	16.7	13	2	6.0	14.0
As ₂ O ₃		0.22	0.92		Trace				
MnO ₂		0.09							
ZrO ₂						0.5		3.3	
NiO		0.001							
Sb ₂ O ₃			4.02						
Misc.				0.1			Trace		1.2

^a Schott AG.

^b Corning Incorporated.

^c Schott Duran, Kimble Kimax®, and Kavalier Simax® all share the same composition.

^d International Simple Glass.

^e Generic Borosilicate E-Glass Standard.

^f Combination of Na₂O and K₂O.

^g Combination of MgO, CaO, SrO, and BaO.

^h Combination of CaO, SrO, and BaO.

originally called Pyright but changed to rhyme with the aforementioned Nonex. Along with Pyrex, Schott's Duran and other products developed over the past century are arguably the best known and commercially successful examples from the borosilicate glass family. To this day, they have been used in scientific lab- and kitchenware, thermometers, high-temperature appliances, telescope blanks, X-ray tubes, and many other common products. Hence, what began as a solution to Abbe's request for better optical glass spawned an entire industry as well as numerous intellectual studies of glass physics, chemistry, and processing.

Even a century after its invention, however, a material as ubiquitous as Pyrex remains studied for its structure and properties to improve its understanding [7]. At least from the network-forming cation (boron and silicon) perspective, this structure is readily determined with nuclear magnetic resonance (NMR) spectroscopy (Chapter 1.2). The ^{11}B NMR spectrum (Figure 2) in particular allows for determination of the fraction of tetrahedrally coordinated boron (N_4) and in addition provides evidence for a rich short-range structure composed of multiple B(III) and B(IV) environments. The challenge thus is to make sense of such information to control and optimize glass properties – the next frontier in efficient discovery, development, and commercialization of new borosilicate glass compositions.

2.2 Modern Materials

Resulting from a better understanding of glass leaching and phase separation, another commercial milestone was the development of Vycor glass in 1939 by H. Hood. Phase separation in $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ glasses can be quite extensive (Figure 1). It generally results in a boron- and sodium-rich phase, which is readily dissolved by mineral

acids and leaves behind a primarily silica-rich glass. The porous microstructure can be coarsened with thermal treatment, allowing for a wide range of porosities. Although this porous glass has found many applications, for example, as filters and membranes with pore sizes ranging from 20 to 220 Å, Vycor is more commonly used after heat treatment and consolidation of the porous silica-rich glass: a glass article can thus be generated from an easily melted and shaped alkali borosilicate glass, which, after controlled phase separation and leaching, collapses into a homogeneous glass similar in composition to pure silica. Such an approach circumvents more costly and challenging processing of silica glass into complex shapes. These dense Vycor articles exhibit very low CTE and are thus especially useful in high-temperature applications (e.g. crucibles).

Originally developed in 1940 without incorporation of boron oxide, E-glass was modified in the 1950s to the standard borosilicate composition (Table 1) by Owens Corning Fiberglass Corporation. This product represented another significant milestone in the commercial history of borosilicate compositions, as the market for this type of borosilicate glass has been extensive and long lasting. These fibers have been used primarily as insulation and reinforcing materials (Chapters 1.5 and 9.3), accounting for up to 99% of the commercial fiberglass market [8]. Much of the subsequent scientific and technical work on E-glass fibers has focused on tailoring mechanical properties, increasing their chemical durability, and finding environmentally and energy friendly compositions (Chapter 1.5).

A rather different but significant area of interest/application for borosilicate glasses deals with nuclear waste storage (Chapter 9.10). Vitrification of such waste in borosilicate glass hosts is being used in a number of countries on a fairly large industrial scale. Some estimates suggest that more than 90% of the highly radioactive, heat-producing nuclides from spent fuel are immobilized in borosilicate matrices. The principal concerns and, therefore, research interests pertain to glass corrosion and the ability to store safely these wastes in vitreous form. The better part of five decades of research has focused on aqueous corrosion of these glasses and potential mobilization of the hazardous material. Two fundamental aspects of borosilicate glass corrosion continue to be the initial water diffusion and ion exchange with the borosilicate glasses, as well as network hydrolysis and dissolution (Chapter 5.12). Solution saturation and reprecipitation of crystalline and amorphous materials further complicate the understanding and use of borosilicate glasses in this particular application. Current knowledge and usage include standardized compositions, such as the International Simple Glass (ISG) in Table 1, allowing for broader and more comprehensive research into

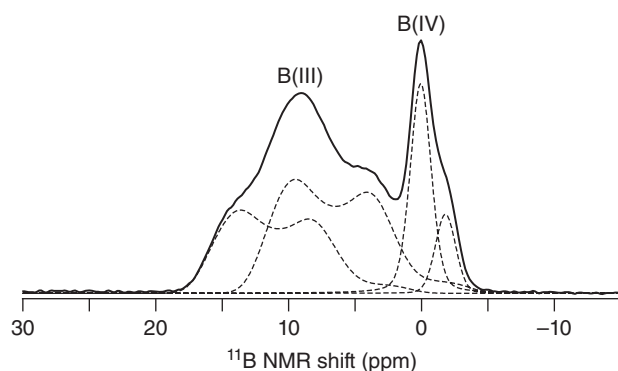


Figure 2 Coexistence of B(III) and B(IV) in Pyrex glass as clearly revealed by ^{11}B MAS NMR spectra (magnetic field of 11.7 T) [7]. Deconvoluted peaks corresponding to multiple B(III) and B(IV) sites are denoted by dashed lines.

borosilicate glasses for nuclear waste immobilization by many different international groups [9].

At this moment, however, the current commercial leader in borosilicate glass products is their use as liquid crystal display (LCD) substrate glasses and as protective cover glasses and touch screens in consumer electronic applications (Chapter 6.9). As shown by some representative examples in Table 1, the majority of these high-tech glasses are based on borosilicates in which additional network modifiers and formers are introduced along with other additives to tailor their properties for specific applications. Corning Code 1737 (Table 1) was developed early in the commercialization of LCD, serving as an alkali-free substrate material for this technology. Today, LCD substrate panels are made with a variety of different borosilicate and related glass compositions and represent one of the largest markets for thin glass sheets (Chapter 6.9). A related new business, with very different material requirements, concerns glasses for handheld consumer electronics such as Corning® Gorilla® Glass, SCHOTT Xensation®, and Asahi Dragontrail® used for protecting covers that are highly engineered by chemical strengthening to survive a variety of possible damaging events (Chapter 3.12).

Although most of the latter products are now made from aluminosilicate glasses, sometimes without the incorporation of boron oxide, some of the early work on chemical strengthening included borosilicate compositions. The chemical tempering, or ion exchange of glass, originally demonstrated with Ag^+ diffusion by Schulze [10] and then with alkali exchange by two groups, Kistler [11] and Acloque and Tochon [12], requires incorporation of some mobile (i.e. exchangeable) species in the glass (Chapter 3.12). Exchange of a smaller cation (e.g. Na^+) with a larger cation (K^+) leads to surface compression and a more damage-resistant glass surface. In general, addition of Al_2O_3 leads to favorable properties such as density and formability, including suppression of miscibility gaps, so boroaluminosilicates tend to be the more commonly developed and utilized commercial glasses for these modern technological applications.

3 Vycor: A Composition–Structure Case Study

Glasses form from pure silica to pure boron oxide in the binary B_2O_3 – SiO_2 system. They are generally well characterized in terms of network structure and other important aspects, including phase separation [13–15]. The latter results from metastable immiscibility and extends as a ternary immiscibility dome in sodium borosilicates (Figure 1). Introduction of small quantities of high field

strength cations (e.g. Li^+ and Ca^{2+}) accentuates the phase separation originally present in binary borosilicate glasses [16].

In early studies, X-ray scattering was used to determine the first sharp diffraction peak, correlating with an average cation–oxygen distance that increases from zero to ~45 mol % silica and is then constant at higher SiO_2 contents. A recent study investigated the contributions of superstructural units (e.g. boroxol rings) to binary borosilicate vibrational density of states and the corresponding impact of this type of structure on thermal properties [17]. In spite of an apparent lack of significant commercial interest in these binary glasses at the present time, some of these compositions have been used in optical fibers and anticorrosive coatings. Sol–gel processing of binary B_2O_3 – SiO_2 glasses has been one particular area of recent study, indicating that truly homogeneous glasses in this binary system can be achieved [18].

That ready vitrifiability frequently coexists in borosilicate glasses with immiscibility and phase separation has intrigued and often frustrated researchers for the past many decades. Perhaps the simplest and most illustrative example is that of ternary alkali borosilicates such as those of the Na_2O – B_2O_3 – SiO_2 system (Figure 1), which includes some of the more famous commercial compositions. As illustrated by Vycor glass, the existence of a large liquid immiscibility dome is not necessarily detrimental, but it can complicate the fabrication process. Hence, one of the interesting and currently relevant questions in such systems is a precise understanding of the microstructure of these phase-separated glasses in terms of either spinodal or nucleation–growth coalescence-type mechanisms (Chapter 5.2).

A deeper understanding of glass structure at both short and intermediate ranges may also aid in understanding phase separation. For example, ^{11}B MAS NMR spectra of Vycor (Figure 3) give insight into the boron atomic environment in the material as it is processed. The spectrum of a heat-treated product, which resembles that of

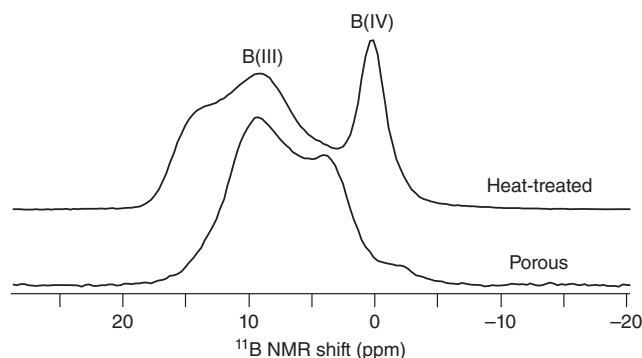


Figure 3 Variations of boron speciation upon processing of Vycor glass shown by ^{11}B MAS NMR spectra (magnetic field of 11.7 T).

the as-made glass but with enhanced phase separation, shows a large fraction, N_4 , of boron in B(IV) groups of about 30 %, reflecting the strong association between boron and charge-compensating sodium. Upon chemical leaching of this heat-treated glass, one obtains porous Vycor whose composition and structure have been significantly altered through elimination of the poorly durable sodium borate phase.

The ^{11}B MAS NMR data actually indicate that the residual boron is found as B(III) units (Figure 3), consistent with the fact that the porous Vycor is a SiO_2 -rich phase containing only a small fraction of B(III) and essentially no modifier. In other words, this glass is a binary borosilicate whose ^{29}Si NMR spectrum (not shown) is mainly composed of Q^4 tetrahedra along with Q^2 and Q^3 silicate groups associated with surface silanol groups, which can be substantially reduced, or even eliminated, with further heat treatment and consolidation into a dense glass. As a simple conclusion, one can thus state that a technique such as NMR depicts the main steps involved in the formation of porous Vycor glass in such a way as to enable researchers to design and optimize the phase separation and leaching processes and, thus, to control accurately the composition, microstructure, and properties of the material.

4 Structural Aspects

4.1 Fourfold Coordinated Boron

The relatively simple $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses are representative of many borosilicates. Their network structures have been examined with a wide variety of tools (NMR, Raman, neutron scattering, X-ray diffraction, etc.), which has resulted in structural models accounting for three- and fourfold coordinated boron or nonbridging

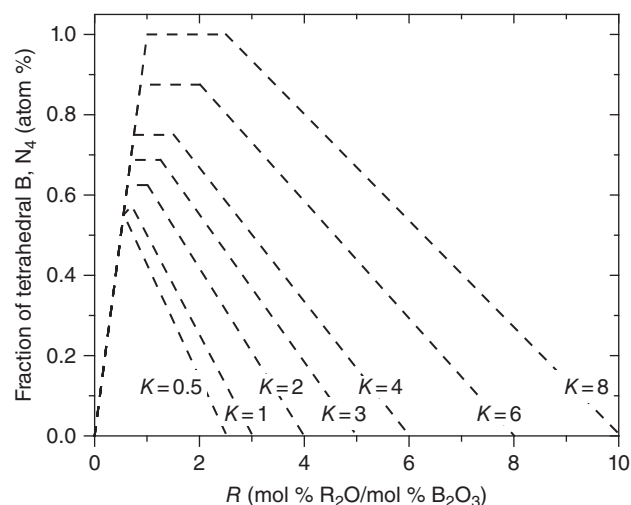
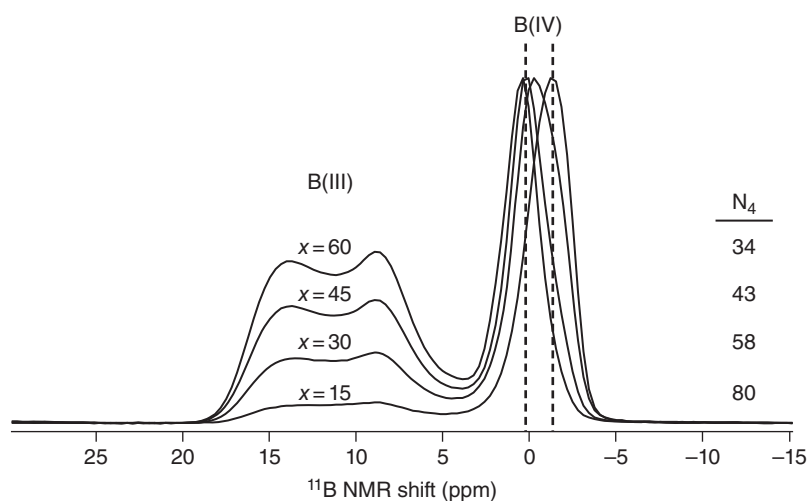


Figure 4 Compositional dependence of fourfold coordinated boron in alkali borosilicate glasses according to the model of Dell et al. [19]. Fraction of tetrahedral boron, N_4 , plotted as a function of $R = \text{R}_2\text{O}:\text{B}_2\text{O}_3$, dashed lines representing the impact of $K = \text{SiO}_2:\text{B}_2\text{O}_3$ on these values.

oxygen (NBO) on silicon (Chapters 2.1 and 2.4), as well as for properties of these glasses, including the contributions of B(IV) groups and overall network polymerization toward lowering thermal expansion. A very influential model was based by Dell et al. [19] on pioneering ^{11}B NMR work to predict the fraction of B(IV) as a function of both modifier content and $\text{SiO}_2:\text{B}_2\text{O}_3$ ratio (Figure 4). It assumes that each sodium added induces the conversion of a BO_3 trigonal unit into a BO_4 tetrahedron, consistent with the fact that B_2O_3 -rich glasses typically contain a significant fraction of both polyhedra as indicated by the relative ^{11}B peak intensities in NMR spectra (Figure 5). For $x = 60$ in Figure 5, the observed N_4 value, slightly higher than 0.3, agrees with the model predictions

Figure 5 Effect of Si-B substitution on boron speciation in $17 \text{ Na}_2\text{O} \cdot x \text{ B}_2\text{O}_3 \cdot (83-x) \text{ SiO}_2$ glasses on ^{11}B MAS NMR spectra (11.7 T). For each composition, the N_4 value is given to the right in the same order as for x . Resonances from B(III) and B(IV) groups are denoted, along with the peak positions for two distinct types of B(IV) environments (dashed lines) [20].



[19] made from the parameters $R = 0.3$ and $K = 0.3$ characterizing this particular composition (Figure 4). A similar agreement for N_4 of about 0.77 is found for the $x = 15$ glass with the predictions made for $R = 1.33$ and $K = 4.33$. Even though it is nearly 40 years old, the Dell et al. model thus remains valid for a variety of borosilicate glasses, especially at modest R and K values. The trends in N_4 predicted by such a model are also consistent with physical property trends, in that an important characteristic of these glasses, namely, the thermal expansion, is controlled by the degree of polymerization, which depends directly on the concentrations of B(IV) and NBO. The competition between these two structural features upon addition of modifier oxide opposes a tetrahedrally coordinated network-forming cation (e.g. B(IV)) to a depolymerized silicate group having fewer than four covalent linkages to other network formers, thus involving a large impact on local topology of the glass.

For larger values of these ratios (e.g. $R > 1$ and $K > 8$), however, the model predicts N_4 values of 100%, which would mean that all boron atoms are in fourfold coordination. But actual ^{11}B NMR-derived N_4 values are always lower than 100% because these high modifier (Na_2O) concentrations eventually lead to the creation of NBO on silicon atoms instead of additional B(IV) groups. The competing role of charge-balancing cation and network modifier exhibited by Na^+ is even more complicated for other modifying oxides, especially for the alkaline earth cations, for which multinuclear NMR data have shown that cation field strength dictates the extent of B(IV) charge balancing by the modifier [21, 22]. As a result of these changes in network structure with different modifiers, the physical properties of such borosilicate glasses are also impacted, with fewer B(IV) groups and a larger number of NBO leading to network depolymerization, a drop in T_g , and a negative correlation between CTE and boron speciation. Although new models

have been designed to allow for a more random distribution of modifiers between the borate and silicate groups [21, 23], they do not predict accurately enough the boron coordination, especially when additional network-forming cations (e.g. Al_2O_3 or P_2O_5) are added. Further characterization and model development are thus necessary to understand better the short-range structure in these glasses.

4.2 Silicon–Boron Mixing

The manner in which network-forming silicon and boron mix can also be investigated by ^{11}B MAS NMR spectroscopy. For glasses with similar amounts of Na_2O (Figure 6), the impact of $\text{SiO}_2 : \text{B}_2\text{O}_3$ ratio is reflected by the measured N_4 fraction. As predicted by structural models (e.g. Figure 4), the coordination of boron is mainly determined by the $\text{R}_2\text{O} : \text{B}_2\text{O}_3$ and $\text{SiO}_2 : \text{B}_2\text{O}_3$ ratios. Compositions with high K values, such as that of Figure 6b, allow for much larger N_4 values caused by mixing of the silicate and borate polyhedra, driven perhaps by relaxation of B(IV) avoidance (i.e. avoidance of B(IV)–O–B(IV) linkages) that is important for glasses containing higher amounts of B_2O_3 (e.g. lower K values).

Mixing of silicate and borate polyhedra is not necessarily ideal, however, so some B(IV)–O–B linkages are evident from the appearance of a second B(IV) resonance in these glasses. One resonance at approximately -1.4 ppm (Figure 6b) is assigned to B(IV) with four silicon next-nearest neighbors (NNN). Owing to the low SiO_2 content of this particular glass, some of the B(IV) are surrounded by fewer Si NNN, the difference being at least one B NNN. The peak at $+0.2$ ppm in Figure 6b is B(IV) with 3Si and 1B NNN. As shown for Pyrex in Figure 2, multiple B(IV) peaks resulting from ordering between boron and silicon are important and common features for borosilicate glasses. The relative population,

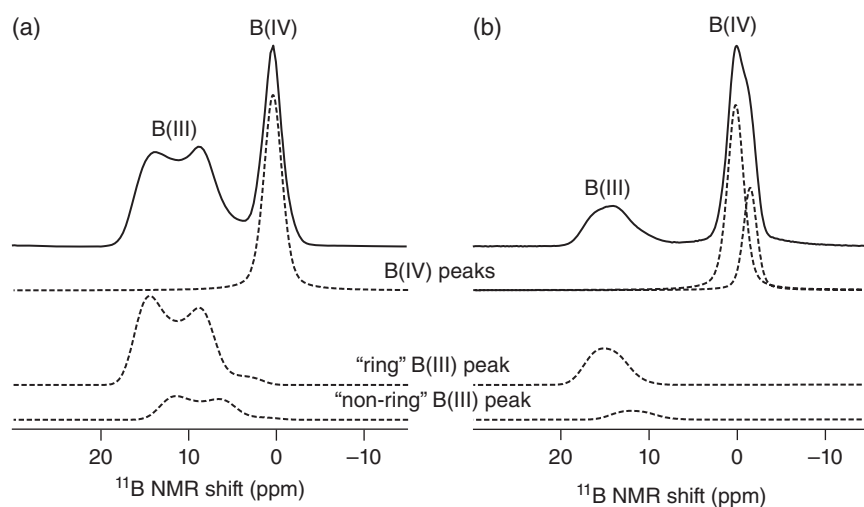


Figure 6 ^{11}B MAS NMR spectra for (a) a boron-rich glass with composition $17 \text{ Na}_2\text{O} \cdot 60 \text{ B}_2\text{O}_3 \cdot 23 \text{ SiO}_2$ measured at 11.7 T [20] and (b) a silica-rich glass ($20.4 \text{ Na}_2\text{O} \cdot 21.7 \text{ B}_2\text{O}_3 \cdot 57.8 \text{ SiO}_2$) measured at 16.4 T [24]. Solid lines are the experimental NMR data, and dashed lines represent simulations of the various B(III) and B(IV) components, as labeled.

or extent of mixing between B and Si, is very sensitive to glass composition because B(IV)(4Si) is predominant in silica-rich glasses, in contrast to glasses having higher concentrations of B₂O₃, where more B(IV)–O–B linkages (e.g. B(IV)(3Si,1B) units) are common, as shown by the changes in B(IV) peak position with varying *K* in Figure 5.

From a practical standpoint, mixing of B³⁺ and Si⁴⁺ in the anionic framework, made possible by association of boron with charge-compensating cations such as alkali ions, has important consequences. When added to silicates, B₂O₃ causes large freezing point depressions because of its very low melting temperature of 712 K, an effect that is still enhanced by the entropy of Si–B mixing. This is the reason why homogeneous glasses are obtained at lower temperatures for borosilicates than for silicates. The effect is similar to that yielded by addition of alkali oxides to silicates, but it has the important advantage of not affecting significantly the polymerization state of the material and, thus, not degrading its stability.

4.3 Superstructural Units

Another widely debated topic is the occurrence of superstructural units in the network. Six-membered rings composed of B(III) and B(IV) polyhedra (and their associated bridging oxygens) are ubiquitous in alkali borate glasses, as shown by NMR and Raman spectroscopies or other structural probes. In borosilicate glasses, some of these ring structures are thought to form through incorporation of both silicate and borate polyhedra, as in the minerals danburite [CaB₂(SiO₄)₂] and reedmergerite [NaBSi₃O₈]. As characterized by such well-defined superstructural geometries, this type of intermediate-range structure is apparently unique to borate and borosilicate glass families. Its identification is particularly effective with ¹¹B NMR and Raman spectroscopies.

As seen for Pyrex (Figure 2) and other borosilicate glasses (e.g. Figure 6), the ¹¹B MAS NMR spectra contain considerably more information than simply on boron coordination numbers. As discussed for B(IV) peaks, the presence of multiple B(III) resonances is reflective of multiple structural environments involving BO₃ polyhedra. This feature has been studied not only with ¹¹B MAS NMR but also with ¹¹B dynamic-angle spinning (DAS), double-rotation (DOR), and multiple-quantum magic-angle spinning (MQMAS) NMR spectroscopy. The fits made to the spectra (not shown) generally yield two distinct B(III) species having similar quadrupolar coupling parameters, but differing significantly in their isotropic chemical shifts. This chemical shielding difference of 3–4 ppm was first measured in glassy B₂O₃ and attributed to boroxol ring and non-ring B(III) units [25]. The multiple B(III) peaks detected in ¹¹B NMR

experiments, like in the examples herein, have been consistently interpreted in terms of ring and non-ring B(III) species: the ring peak represents B(III) units in boroxol and modified rings (e.g. tetraborate, triborate, danburite, etc.), whereas the non-ring B(III) environment includes those of BO₃ polyhedra that exist outside of these well-defined superstructural units.

Over broad compositional ranges, the presence of ring-type B(III) indicates that the borosilicate glass network is characterized by a surprising amount of short- and intermediate-range order. These features have important implications for network topology and the nature of the network-forming species that control the physical and mechanical properties of the glass. One of the ongoing challenges in this field is the identification and absolute confirmation of different network polyhedra and ring structures in highly modified borosilicate glasses. For those glasses containing NBO, especially when these are bonded to boron atoms, the complexity in their NMR and vibrational spectra is significantly increased. In addition to the possibility of ring and non-ring B(III) units, as well as of multiple types of B(IV) polyhedra based on mixing between B and Si units, the presence of metaborate units (B(III) with a single NBO) would appear as yet another B(III) resonance in the ¹¹B NMR data. The combination of multiple spectroscopies, and possibly new advances in NMR methodology, should yield better and more precise descriptions of these complex glass structures.

4.4 From NMR to Integrated Studies

To begin with oxygen, other nuclei amenable to NMR experiments are incorporated in borosilicate glasses. In particular, ¹⁷O NMR has been used to understand the network connectivity between borate and silicate groups, lending in this way support to the characterization of phase separation in binary B₂O₃–SiO₂ glasses and to a detailed understanding of topological disorder and phase separation in multicomponent borosilicates [14, 26]. Additional NMR studies have dealt with ²³Na, ⁶Li, ⁷Li, ¹³³Cs, ⁴³Ca, and ²⁵Mg modifier cations, allowing researchers to understand the local environment of these components, as well as the impact of such modifiers on the network structure and properties of borosilicates of academic or commercial interest. In this respect, Na⁺ and Li⁺ are two modifiers of significant interest in model systems and in the development of better structure–property relationships that are important in commercial glasses utilizing ion exchange for mechanical toughening (Chapter 3.12).

Although NMR has become one of the mainstream characterization tools for network structure, other spectroscopies and computational methodologies have been

extensively developed to learn about the physics and chemistry of borosilicate glasses. Vibrational spectroscopies, for example, continue to play a key role in understanding the network structure of borosilicate glasses. Starting with the seminal work of Konijnendijk [27], Raman spectroscopy has been instrumental in developing and contrasting structural models for borosilicates with those designed for borate and silicate glass families, for instance, with respect to danburite and reedmergnerite superstructural units [28, 29].

Whereas knowledge of the structure of borosilicate glasses has been significantly advanced over the past 50+ years, a precise description of short- and intermediate-range network structure, including mixing of the two glass-forming oxides, continues to be a challenge in both experimental and theoretical approaches. Some of the more recent advances in this arena involve a combination of experimental and modeling studies whereby empirical models are for instance complemented by theoretical calculations of NMR spectra or molecular dynamics (MD) simulations [30]. Purely computational approaches also are common and have yielded potentially important insight into these issues. As advanced during the last past decades, MD simulations have been validated in terms of reproducing boron NMR data (i.e. N_4 values) and other structural details obtained by spectroscopic investigations (Chapter 2.8).

4.5 The Impact of Al_2O_3

In addition to these studies on relatively simple glasses, much experimental work has been devoted to the effects of additional glass formers on structure and properties. As a crucial component of new products, Al_2O_3 has been extensively investigated because the presence of such a third glass former complicates the interactions between modifiers and both B_2O_3 and SiO_2 . The ratio of modifier to Al_2O_3 in these boroaluminosilicates actually controls many properties, including density and T_g . These features and the concomitant changes in the glass structure have been elucidated primarily by means of multinuclear NMR techniques [31, 32].

In fact, addition of Al_2O_3 also requires charge-compensating cations to stabilize Al in tetrahedral coordination, which lowers the fraction of network-modifying cations. As a consequence, the NBO content decreases and, if the glass is highly modified, also reduces the N_4 fraction. The resulting glass network may exhibit more connectivity, in particular if Al_2O_3 addition reduces or eliminates NBO on both boron and silicon. In glasses containing few modifiers, for example, below the Dell et al. critical R^* value [19], then boron is typically converted from tetrahedral units back to trigonal species.

This transformation has of course a large impact on glass properties.

Current understanding and related empirical models of boroaluminosilicate glasses often consider simplified interactions between modifiers and network formers by assuming that Al_2O_3 is preferentially stabilized in AlO_4 units, with any “excess” modifier then made available for other structural changes. This assumption appears to hold generally for a great many systems, but may not be exact, so models based on this view would also be inaccurate. Recent work on boroaluminosilicates conducted by several prominent research groups does indeed show that all Al is not necessarily in fourfold coordination in charge-balanced compositions. The presence of a non-zero AlO_5 population, which may also be sensitive to fictive temperature and compression of the glass, suggests a more complicated interaction between network modifiers and formers in these multicomponent borosilicate glasses. This topic thus continues to be an active area of research. Advances in both experimental and computational study will result in a better structural understanding of glass formation and properties, perhaps also leading to additional commercial and scientific opportunities.

5 Temperature and Pressure Variations of Network Structure

5.1 Temperature vs. Entropy

With rising temperature, the structure of a melt necessarily varies so as to ensure an increase in configurational entropy. In borosilicates, changes in boron speciation are a simple way to fulfill at least partially this requirement. Particularly in highly modified glasses [21], one can actually shift markedly the equilibrium between B(IV) and NBOs by varying the quenching rate to freeze the short-range structure at different fictive temperatures (Figure 7). Although the largest impact of T_f is on boron speciation, a modification of the line shape apparent on closer examination of B(IV) peaks (Figure 7) indicates more complicated changes in the network structure. The quenched glass has at least two types of B(IV) that are not well resolved in the 11.7 T spectra but are nonetheless indicated by the noticeable asymmetry of the B(IV) peak. Annealing induces a slight increase of the relative intensity at the upfield (more negative shift) side of the peak, which one would assign to B(IV) surrounded by 4 Si NNN. If this intensity change is meaningful (e.g. reproducible and outside of the measurement uncertainty), then such data indicate that a change in thermal history for this glass causes an overall increase in N_4 .

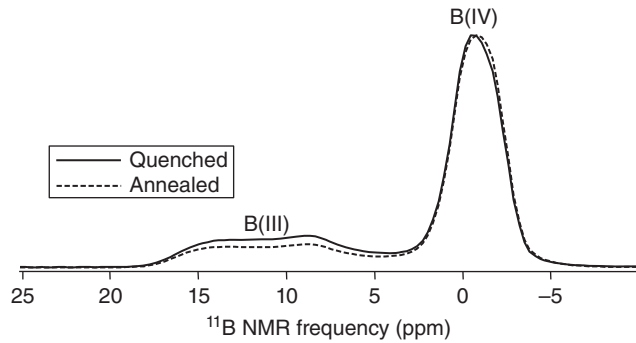


Figure 7 Increase in the B(IV) fraction in a sodium borosilicate glass upon annealing of a quenched glass, shown by a comparison of ^{11}B MAS NMR spectra (11.7 T) [33].

much of that change not affecting equally all B(IV), but mainly those surrounded by 4 Si.

A closely related area of significant interest, but rather challenging to study with traditional characterization tools like NMR, is the structure of borosilicate melts and supercooled liquids. Most of the commercially relevant borosilicate glasses are processed from melts, so it stands to reason that a deeper knowledge of glassmelt properties and structure would be immensely beneficial. Some *in situ* methodologies do exist and have been used to characterize glassmelts, but even high-temperature NMR and other spectroscopies are difficult to implement and are generally restricted to specialized laboratories. One area of growing utility and popularity relates to optical interrogation of glassmelts, involving small furnaces, laser heating, and laser heating with aerodynamic levitation. These methods provide a means by which to use Raman and Brillouin light scattering, neutron diffraction, and high-energy X-ray scattering to study glassmelt chemistry and physics (Chapter 2.2). In a recent neutron diffraction examination of boron coordination in borosilicate melts, dramatic decreases in N_4 on melting two borosilicate glasses were, for instance, observed, such structural insight having then

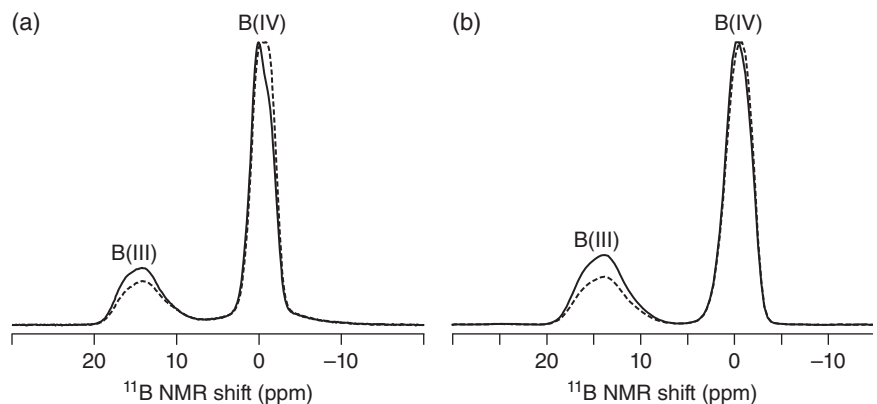
been discussed in the context of the structural underpinnings of melt viscosity [34].

5.2 Pressure vs. Volume

With increasing pressure, the structure of a melt necessarily becomes more compact to ensure the thermodynamically required density increase. For obvious reasons, the effects have been well documented for glasses of geochemical interest whose network structure has indeed been found sensitive to pressure. Hence, it should not come as a surprise that these investigations have recently been extended to borosilicate glasses. One particularly recent study, using NMR to understand changes in glass structure, but, more importantly, to correlate pressure and short-range structure with glass properties, indicates that certain changes with modest pressure may be irreversible [35]. To illustrate better the changes in glass structure with pressure, ^{11}B MAS NMR spectra have been obtained on two borosilicate glasses before and after high-temperature compression at T_g and 1 GPa. In both glasses (Figure 8), the impact of compression on boron speciation is an overall increase in N_4 , much like the changes in structure with thermal history alone.

In addition to N_4 variations, a preferential change in the type of B(IV) is indicated for the sodium borosilicate glass (Figure 8a), as found for similar glasses having different thermal histories. Here, the peaks assigned to B(IV) with 3 Si, 1 B, and 4 Si NNN, B(IV)(3Si1B), and B(IV)(4Si), respectively, change differently upon compression, with a larger increase in the B(IV)(4Si) concentration. Closer examination of the B(III) region of these spectra gives additional insight into related changes in ring and non-ring B(III) peaks with compression – something that is currently the subject of a combined NMR and Raman study of borosilicate glasses under permanent densification. One of the other structural responses to this high-temperature compression relates to the modifier environment. As mentioned earlier, NMR studies of ^{23}Na (or

Figure 8 Effects of permanent densification on the boron speciation of two borosilicate glasses, as shown by the differences between the ^{11}B MAS NMR spectra (16.4 T) recorded for the as-made glasses (solid curves) and compressed samples at T_g and 1 GPa (dashed curves). (a) 20.4 Na₂O·21.7 B₂O₃·57.8 SiO₂ [24]. (b) 15.0 Na₂O·10.1 CaO·16.5 B₂O₃·58.4 SiO₂ [36].



other modifiers) allow one to follow changes in the local environment of these cations as glasses are densified. Many NMR studies have shown a clear increase in chemical shift of ^{23}Na for glasses densified by compression either at room or at elevated temperatures. Most of these data have been interpreted as a general reduction of the average Na—O distance in the densified glasses and not as a change in the coordination number of the alkali. Further understanding of both the glass network and the modifier environments, using advanced experimental and computational methodologies, is necessary to describe fully densification of borosilicates under high pressure and possibly during mechanical damage induced by nano- and micro-indentation.

6 Perspectives

In spite of almost two centuries of study, borosilicate glasses remain intriguing materials whose incredible commercial success justifies the widespread research efforts made to characterize them better and improve their structure–property relationships. Accurate determinations of glass structure across several length scales (short and intermediate range) will continue to drive new applications as it will be difficult to optimize compositional and processing variables, including temperature and pressure, without this information.

The next wave of innovation is actually underway: it is the development of ultra-strong glasses through better characterization of bulk and surface structure and properties [37]. Of particular importance in this respect are the details of flaw generation, crack growth, and overall glass durability and, in turn, the impact of these phenomena on glass structure and properties [38]. Applications of borosilicate glasses are also growing into new scientific and commercial areas, for example, in glass/polymer laminates or in biological uses. Hence, the surfaces of these materials become critical in their applications, driving the need for enhanced understanding and control of surface chemistry and properties, as well as of glass dissolution mechanisms.

In all these respects theoretical simulations will also be valuable. The interatomic potentials needed in MD simulations have thus been improved to yield correct structures and properties over wide ranges of composition. But the main difficulties remaining to be overcome concern the temperature sensitivity of cation coordination and the unrealistically high quench rates currently possible.

Advances in experimental and computational methodologies to understand and control better phase separation in borosilicate glasses may also lead to new and improved compositions. Even today, the development

of new NMR and transmission electron microscopy (TEM) capabilities have increased our ability to discern phase separation in glasses, which either account for or aid in understanding associated physical properties, as well as serve to understand better nucleation and crystallization in glasses.

Finally, many challenging problems in glass science will benefit from the study of model borosilicate systems. A deeper understanding of the glass transition, intermediate-range structure, phase separation and crystallization processes, impact of temperature and pressure on glass structure and properties, etc. is continually achieved through work on borosilicate glasses. Progress in new and advanced simulation approaches and experimental capabilities will also lead to an improved understanding of these important aspects of glass science.

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7.7

Glass for Pharmaceutical Use

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1 Introduction

One of its properties that originally made glass a highly prized material was its inertness with respect to liquids and other substances that it could contain (Chapter 10.2). The small vials for perfumes and unguents made as soon as bulk glass was produced in the late Bronze Age are a clear testimony of this ancient recognition. When it became common in the eighteenth century, the use of glass that for the storage of dry and liquid pharmaceuticals was thus the continuation of an extremely old tradition. Even though it has since then been replaced by plastics or other materials in a great many applications, glass has kept fundamental advantages in terms of chemical inertness, lack of porosity, shapability, transparency, coloration, or possibility of high-temperature sterilization. As a result, the use of glass in pharmacy keeps increasing, especially for new applications such as pre-filled syringes, which are the primary way for delivering new high-technology drugs.

The purpose of this chapter thus is to review the main features relevant to the use of glass in pharmacy. The pharmacopeial requirements for containers are first considered and a definition of the most common glass types provided. The current glass-tubing production processes are then presented, as well as the conversion steps to obtain containers from glass tubes. Next the factors affecting the mechanical resistance of the containers are briefly examined with a particular focus on the effects of glass forming and handling on the packaging performances. The chemical resistance of glass has important implications for the storage of pharmaceuticals. Hence,

possibly significant interactions between the container internal surface and the enclosed therapeutic agents are reviewed, with some considerations from the perspective of glass manufacturers. An account on the current internal and external treatments to improve the chemical and mechanical performances of the containers is provided. Finally, the chapter will examine some high-technology perspectives on the future of glass containers for parenteral uses (i.e. subcutaneous or intravenous injections), focusing on innovative solutions aiming at improving the patients' quality of life.

2 Glass Products and Types

Typical containers for pharmaceutical use are ampoules, vials, syringes, and cartridges (Figure 1):

- *Ampoules* remain the less expensive products available on the market. Their use keeps slightly increasing worldwide in that a growth in China, Japan, and other Asian countries compensates for a decrease in Western Europe and North America.
- *Vials* show a constant increase, growing in all markets because of their universal acceptance by end users and pharmaceutical companies. Such an increase is tightly connected to a quality improvement in terms of increasing output, lower rejection rates, and decreasing cosmetic defects.
- A high growth is shown by *cartridges* in all applications, whether dental, biotechnological, and insulin related. In the last case the so-called pen applications for self-administration are key success factors, but the highest quality is then requested in terms of cosmetic defects and dimensional tolerances because of the high cost of such drugs and the need to guarantee a very precise dosage.

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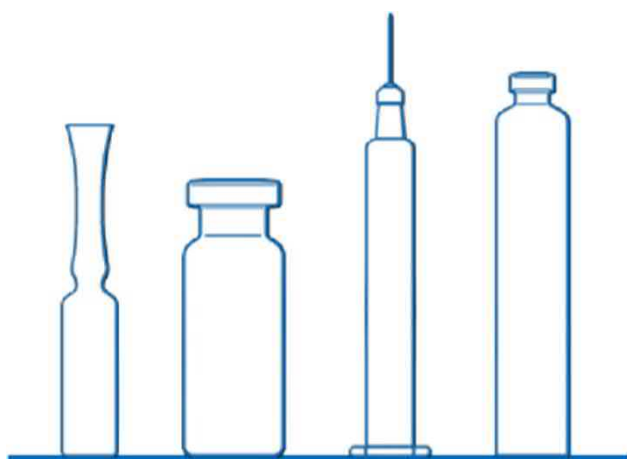


Figure 1 Different glass container types: ampoule, vial, syringe, and cartridge from left to right.

- The high growth of *syringes* production is driven by prefilling. Thanks to their ease of use and dosage accuracy, these containers are already the primary packaging of choice for many healthcare users. Their major markets are either key therapies that include vaccines, low-molecular-weight heparins, biotech products or applications in combination with auto-injectors.

The use of glass for pharmaceutical preparations is ruled by pharmacopeia authorities. The European [1] and US pharmacopeias [2] acknowledge two different types of glasses, namely, *neutral borosilicate* and *soda lime*, and three different types of glass containers according to a well-established classification based on their hydrolytic resistance (Chapter 5.1). In order of decreasing cost, these are the following:

- *Type I glass containers* are made of neutral borosilicate glass, which have intrinsically a high hydrolytic resistance. These containers can thus be used for any purpose.
- *Type II glass containers* are usually made of soda-lime glass. Being subject to alteration by contact with aqueous solutions (Chapter 5.11), they can be internally treated over a thickness of about 0.5 μm to acquire a hydrolytic resistance equivalent to that of type I glass. These containers are suitable for acidic and neutral aqueous preparations for parenteral use.
- *Type III glass containers* are made of untreated soda-lime glass. Owing to their moderate chemical resistance, they are suitable in parenteral use only for nonaqueous preparations.

The general segmentation of the overall 35–45 billion glass containers produced yearly would indicate a large preponderance of ampoules (Figure 2). In terms of value

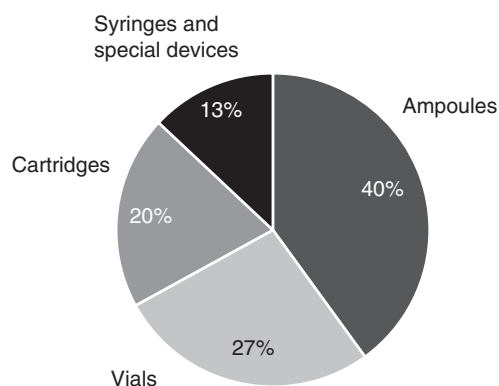


Figure 2 Distribution of pharmaceutical glass containers in terms of production volume.

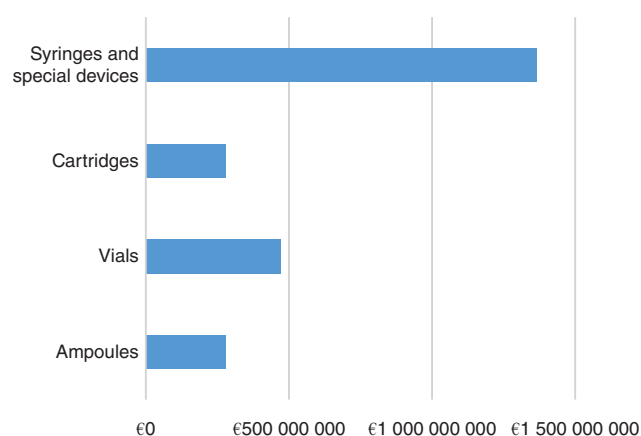


Figure 3 Segmentation of the value (€) of the different container types, year 2017.

as expressed in euros (Figure 3), syringes and special devices generate in contrast the highest revenues, whereas ampoules provide the lowest, clearly illustrating the value added in the highly engineering part of the production.

3 Production of Pharmaceutical Glasses and Containers

Pharmaceutical containers are produced from type I and III glasses in the compositional ranges shown in Table 1. Coefficients of thermal expansion (CTE) range from 49×10^{-7} to $55 \times 10^{-7} \text{ K}^{-1}$ for clear glass and from 52×10^{-7} to $54 \times 10^{-7} \text{ K}^{-1}$ for amber glass (Chapter 6.2), whereas the working points lie between 1145 and 1165 $^{\circ}\text{C}$ for the former and between 1120 and 1165 $^{\circ}\text{C}$ for the latter, with annealing temperatures ranging from 535 to 575 $^{\circ}\text{C}$. Type I clear glasses includes also high-borosilicate glasses (the

Table 1 Composition ranges of type I and III pharmaceutical glasses (type II same as type III).

Oxide (wt %)	Type I		Type III
	Clear tubing	Amber tubing	Molded
SiO ₂	72.0–75.0	69.0–71.0	69.0–75.0
B ₂ O ₃	10.0–11.5	7.0–10.0	0–1.0
Al ₂ O ₃	5.0–7.0	5.0–6.0	0.5–4.0
Na ₂ O + K ₂ O	7.0–8.5	7.0–8.0	12.0–16.0
CaO + BaO + MgO	0.5–3.0	2.0–3.0	10.0–15.0
Fe ₂ O ₃		0.5–1.0	
TiO ₂		2.5–3.0	

so-called Exp.33 glasses), thus having higher boron and silica contents and lower alkali contents with a CTE of about $33 \times 10^{-7} \text{ K}^{-1}$. Of course, knowledge of these parameters is of primary importance for the manufacturing process.

3.1 Glass-Tubing Production

Glass tubes or canes are produced with either the Danner or the Vello process (Figure 4). In both processes the starting point is the furnace where raw materials of the glass batch are melted. As a continuous flow, the melt then is shaped as a tube [3]. After these steps the tubing is gauged, classified for use, and cut into the desired lengths.

Named after Edward Danner who was working in the 1910s at Libbey Glass (Toledo, USA), the former can make tubing of 1.6–66.5 mm in diameter and rods of 2.0–20 mm in diameter at drawing rates of up to about 7 m/s for the smaller sizes and with a maximum daily production of up to 40 tons for the largest diameters. With this process, an angled rotating sleeve allows the introduction of air to inflate the tubing. The glass flows at about 1200 °C from the forehearth on a rotating, hollow,

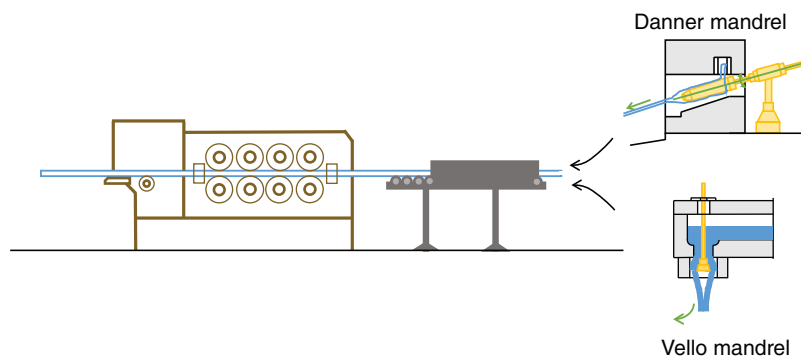
water-cooled mandrel. The outside diameter and the thickness of the finished tubing are then controlled at about 900 °C by the flow of inflating air together with the drawing and rotation speeds and the inclination of the mandrel, which is usually 15–20° from the horizontal.

Named after Leopoldo Sanchez-Vello, the second process was first patented in 1929 in France. In this case, the glass flows from a forehearth into a reservoir in which a hollow bell-shaped mandrel rotates in a ring that allows the glass to flow via the annular space to give a continuously emerging tube. Air is fed via the end of the bell where there is a hollow tip. The dimensions of the tubing are controlled by the rate of draw, the clearance between the bell and the ring, the rate of drawoff, and the pressure of the blowing air. Production rates can be twice as high as with the Danner process, so the size of the drawing line is also much longer to reach from 100 to 140 m.

3.2 Container Production from Tubing

Glass vials can alternatively be produced by blow molding of glass gobs as described in Chapter 1.5. Only the glass-tubing converting technology will thus need to be described here. From tubing to vials the forming process with vertical converting machines is shown in Figure 5 in a clockwise sequence: (i) opening of tubing bottom, (ii) forming of the vial shoulder, (iii) forming of the vial mouth, (iv) cutting of the tubing, and (v) forming of another vial bottom. The whole forming process of vials and ampoules is realized by gas burners, whereas it also includes a thermal shock cutting phase for cartridges and syringes.

These steps are of course part of the production procedure in a long production line (Figure 6) beginning with the feeder that supplies the converting machine with the glass tubing and ending with a fully automated system for quality checking. Specifically, the correct shape of the container is monitored at every step by a camera system that allows for self-adjustment operations in the case of small dimensional deviations. From the machine, the container is transferred to another line where its

Figure 4 The Danner and Vello glass-tubing processes, drawing glass horizontally and vertically, respectively.

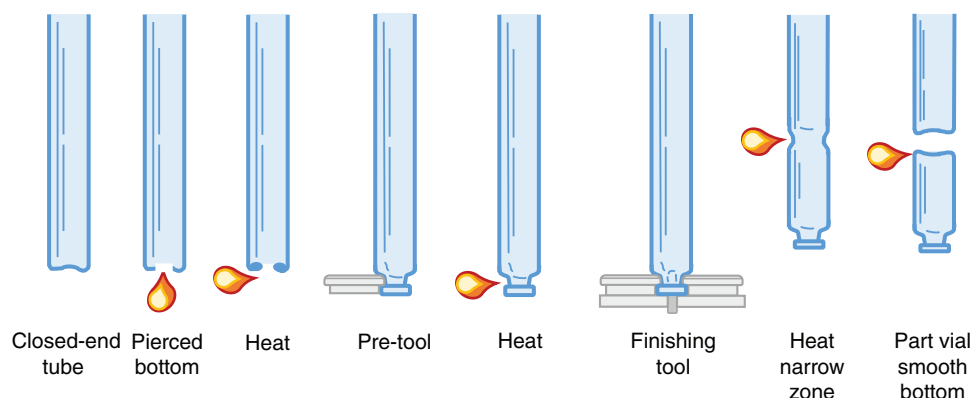


Figure 5 Forming process from glass tube to vial. The various steps include glass heating and processing with pre-finishing and finishing tools.

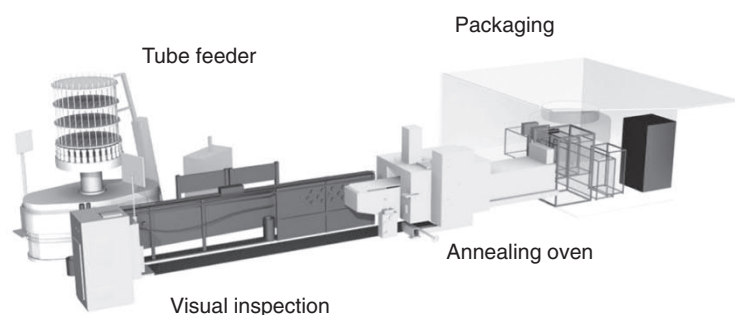


Figure 6 Schematic representation of a glass container production line. Different manufacturing and inspection systems are shown, including a tube feeder, a rotating manufacturing stage, optical inspection devices, and an oven.

dimensional parameters are again controlled by optical and mechanical means. Where appropriate, before being annealed it is then subjected to additional operations according to the customer requirements such as washing, sulfur treatment, etc. Finally, the container is brought to an automatic packing machine, which is confined in a protected clean area, where the final optical control for cosmetic defects is performed.

This factory quality control is the key to guarantee the compliance of the final product with the specification requirements established by both the pharmacopeia and the pharmaceutical industry. Maximum care thus is taken in the converter operations to avoid scratches on the container body. Likewise, special precautions are taken in the machine feeding phase, and all container transfer and packaging operations are performed by robots.

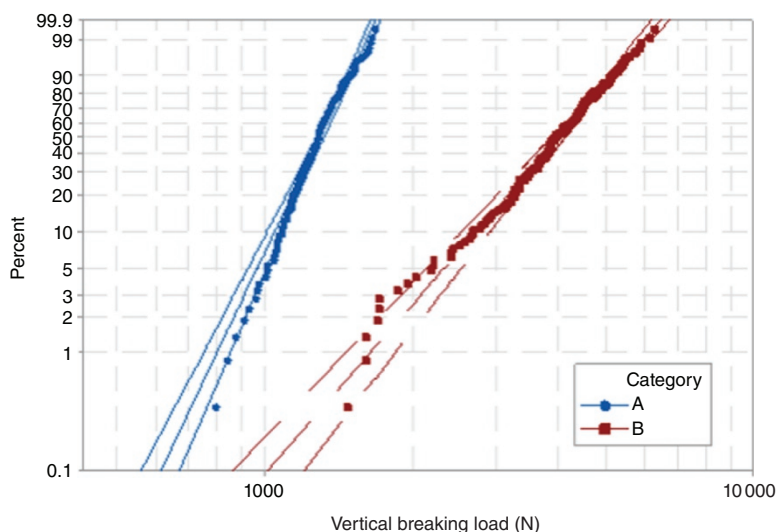
4 Physical Resistance

The theoretical strength of a material is directly connected to the strength of its structural chemical bonds (Chapter 3.11, [4]). In silicate glasses, strong covalent

bonds are present, such as Si—O bonds with energies of about 400 kJ/mol. These features translate into very high theoretical strengths, which could be greater than 10 000 MPa for glasses and glass ceramics. But commonly used glasses have mixed covalent (strong) and ionic (weak) bonds and, moreover, present dispersed structural microheterogeneities. As a result, the theoretical tensile strength of borosilicate glasses can vary from 6500 to 9000 MPa. These values can never be met in practice since the actual strength of glass articles is substantially affected by the presence of surface flaws (Chapter 3.11). Indeed, contact with metal tools or other glass items often causes damages on the surface of glass articles. These surface flaws usually appear as scratches or micro cracks, which act as stress concentrators during mechanical loading.

Eventually, the mechanical stresses generated by these defects may result in breakage of the finished container. Owing to wear and manufacturing processes, these flaws are common in all materials, but their effects are mitigated in ductile materials by plastic flow, which relieves the stress concentrations. Under typical operating temperatures and timescales, however, glasses are brittle materials that display negligible plastic flow. As a consequence, surface defects induced by wear, friction sliding,

Figure 7 As apparent in a probability plot for vertical breaking of cartridges, the considerable improvement in mechanical properties of cartridges produced in a *no-glass-to-glass* line (right) with respect to a standard production (left).



and impacts significantly decrease the mechanical resistance of glass containers [5], so their practical tensile strength is usually about only 20–200 MPa.

Interestingly, the failure of glass products also depends on the loading time and on the area subjected to the mechanical stress. Tensile stresses exerted over large periods of time may cause microscopic cracks to grow and eventually to reach critical sizes. This is why the strength of glass articles is higher for rapid than for slow mechanical loading. In addition, increasing the area subjected to mechanical stress increases the probability of triggering surface flaws, jeopardizing the resistance of the article. All these factors may differ widely from a process to another as illustrated by the considerable differences in vertical breaking probabilities between cartridges produced by two different processes (Figure 7): especially for the “weak” end of the distribution, considerable improvements are obviously provided by the *no-glass-to-glass* line products where the flaws coming from the mutual contact of containers are avoided.

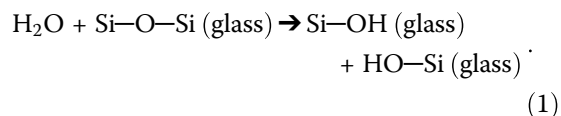
5 Chemical Resistance

5.1 Corrosion Reactions

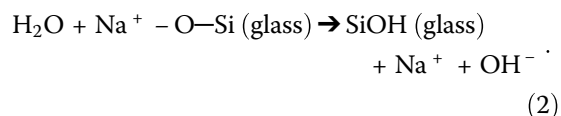
The chemical resistance of pharmaceutical glasses is the resistance to the attack by a liquid medium [6–9]. Although glass is almost inert with respect to the majority of neutral organic media, interaction with aqueous solution causes substantial alterations of the inner contact surface (Chapters 5.11 and 5.12). The resistance to such attacks by aqueous solution is known as the chemical durability or hydrolytic resistance (Chapter 5.1).

The chemical durability of soda-lime commercial glasses has been investigated for nearly a century [10, 11], so the interaction mechanism is well understood. In the field of pharmaceutical glass, borosilicates are recognized as the most durable because their interaction with semi-neutral aqueous solutions does not cause a significant pH shift. The reason is that alkalis are much more tightly bound to the silicate network when present as charge-compensating cations for B^{3+} in tetrahedral coordination (Chapter 7.6) than when being network modifiers as in soda-lime-silica glasses. In other words, borosilicate glasses are properly called *neutral* because the small amounts of alkalis and other ions released by the glass surface do not alter the neutrality of the contact solution.

When an aqueous solution enters in contact with the glass surface, the first stage is the hydration of the contact glass layer according to the reaction



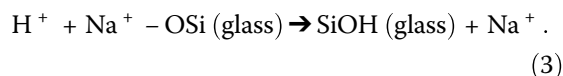
At the same time an ion exchange reaction is initiated between alkali ions in the glass network and proton ions in the leaching solution



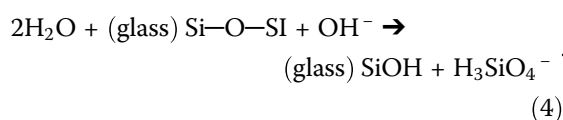
This reaction causes a slight rise of the pH of the extraction solution, which has a negligible effect on the extraction mechanism. The silica gel layer that forms on the surface differs in mechanical properties from the bulk glass. Repeated hydration and dehydration cycles

thus bring to the cracking of such layer and eventual generation of subvisible or visible particles. At this stage the quantity of extracted alkalis linearly correlates with the square root of time (t) but later on the process becomes linear with time (Chapter 5.11). The total extracted amount of alkalis (Q) can be schematically represented by the empirical expression $Q = a\sqrt{t} + bt$, where a and b depend on the glass composition and temperature [10].

For a slightly acidic medium, the following reaction takes place:



With solutions at pH lower than 4, the reaction proceeds up to the formation of an alkali-depleted layer that acts as a barrier toward further attack, whereas the pH remains substantially unchanged. For basic solutions (pH > 9), the OH^- ions break oxygen bridges ($\text{Si}-\text{O}-\text{Si}$ bonds), causing silica to dissolve according to the following dissolution mechanism:



With increasing OH^- concentration, the reaction shifts to the right, thus favoring the dissolution of silicic acid. In addition to pH, time, and temperature, other factors like the surface-to-volume ratio, glass composition, and the contact media determine the extent of chemical attack. For instance, buffers with a strong ionic strength (KCl and citric acid, for instance) or complexing agents such as EDTA, glutaric acid, and phosphate promote extensive interactions with the glass network and cause its total dissolution [12].

5.2 Testing of the Hydrolytic Resistance of Containers

The pharmacopeia distinguish between the resistance provided by the glass itself and that offered by the inner glass surface of the container in contact with water or, more generally, with aqueous preparations.

A *grain test*, carried out on a glass fraction of specified grain size, is suitable to monitor the resistance offered to water attack by the glass as material. In this respect, the distinction between type I and type III glasses becomes obvious when the extract solutions are titrated with a 0.02 M HCl solution after 30 minutes water exposures at 121 °C. The higher quality of borosilicate glasses (type I) manifests itself with a limit of 0.1 ml of HCl solution per gram of glass compared with a value of 0.85 ml for soda-lime glasses (type III). This test can be used also to reveal whether the glass surface has been treated or

Table 2 Comparison between glass grain test results for borosilicate glass tubes and molded soda-lime-silica glasses commercially available.

Supplier	Results (ml 0.02 M HCl/g glass)	Limit value (ml 0.02 M HCl/g glass)
Schott Fiolax	0.037	0.10
NEG BS	0.035	0.10
Nipro	0.036	0.10
Corning	0.036	0.10
Soda-Lime Molded	0.44–0.54	0.85
Soda-Lime Amber	0.53–0.68	0.85

Table 3 Typical surface test results for type I vials produced by different glass-tubing converters using the same tubing raw material.

Vial capacity	Results (ml 0.01 M HCl/ 100 ml extract)	Limit value (ml 0.01 M HCl/ 100 ml extract)	Notes
3 ml	1.1	1.3	Converter A
3 ml	0.70	1.3	Converter B
10 ml	0.70	0.80	Converter C
10 ml	0.55	0.80	Converter B
20 ml	0.27	0.60	Converter B
2 ml	0.39	0.60	Converter C

not and, thus, to distinguish between type I and type II glass containers. In Table 2 typical *grain test* results from commercially available tubing and molded soda-lime glasses are reported.

A *surface test* is mandatorily requested to assess the alkali release from the inner surface of the containers. The latter, filled with water, are autoclaved for one hour at 121 °C, and the pooled extract is titrated with a 0.01 M HCl solution. The limit values are established as a function of container capacities and glass type, being 10 times higher for type III glass containers. Typical *surface test* results on vials of different capacity are displayed in Table 3 where the impact of different converters is also highlighted. In particular cases the individual alkali release can be measured by flame atomic absorption spectroscopy (Chapter 5.1).

5.3 Glass Extractables

There is an increasing attention paid to extractables, i.e. the substances released from the whole drug packaging system after a stress treatment (e.g. autoclaving treatment, long time and high-temperature exposure).

Table 4 Inductively coupled plasma mass spectrometry (ICP-MS) analyses of elements extracted from 10 ml glass type I vials after an autoclaving cycle made according to the *grain test*.

Element	Conc. (mg/l)	Element	Conc. (mg/l)
Cd	<0.01	Sn	<0.01
Pb	<0.01	Ni	<0.01
As	<0.01	Sb	<0.01
Hg	<0.01	V	<0.01
Cu	<0.01	Mn	<0.01
Fe	<0.01	Zn	<0.01
Se	<0.01	Co	<0.01
Ag	<0.01	Au	<0.01
Tl	<0.01	Li	<0.01
Ba	<0.01	Os	<0.01
Pd	<0.01	Pt	<0.01
Rh	<0.01	Ru	<0.01
Cr	<0.01	Mo	<0.01

Several regulations like ICH Q3D and USP <232> have been recently issued on this topic.

These regulations focus the attention on specific elements according to their potential final toxicity. Typical such elements are Cd, Pb, As, Hg, and hexavalent chromium.

Except arsenic, which is sometimes added to the glass batch as a refining agent, none of these elements is intentionally added (Chapter 1.2). They are present in the glass only as impurities in the starting raw materials, most of the times at ppm levels (mg/kg), and find themselves encapsulated in the glass network after melting. Their mobility is almost negligible under normal conditions of use, being extracted only under severe conditions (water at 121 °C for one to two hours, basic extraction at 80 °C for a 24–48 hours, etc.). Thanks to its inertness, glass thus is releasing an extremely limited amount of these elements even after water extraction is performed according to the *surface test* cycle. As illustrated by the data of Table 4, the values found are below the limits of detection of inductively coupled plasma mass spectrometry (ICP-MS), one of the most sensitive analytical techniques used for trace elements (Chapter 5.1).

6 Surface Interactions with Pharmaceutical Products

6.1 General Features

The primary packaging of glass is of paramount importance for parenteral drugs since it represents the first

interface in contact with the therapeutic agent. Different containers interact in specific manners with the drug products depending on their particular shape, the manufacturing process (e.g. forming from glass tubes, internal siliconization), and the assembled components (e.g. plungers, stoppers, needles, etc.). Containers are thus carefully monitored during the entire product shelf life to ensure that the therapeutic characteristics of the drug are not compromised.

Vials have been commonly employed for storage of drugs over long time periods. Under particular conditions, however, the enclosed drug formulation can interact with their inner surfaces. Eventually, this interaction could also lead to glass *delamination*, i.e. the detachment of small lamellae from the glass surface. This potential problem must be specially taken into account for injection systems such as syringes and cartridges, which, as already stated, are becoming more and more common as parenteral packaging solutions thanks to their usability and dosing accuracy. Compared with traditional vials and ampoules, syringes and cartridges in effect differ by the fact that they are exposed to more components with which they could react. As will be described below, the drug compatibility with tungsten, silicone oil, and leachables from stoppers and tip caps, for instance, should be assured throughout the product shelf life.

6.2 Delamination

The appearance of visible glass particles, generally known as flakes (lamellae), in injectable preparations has caused a number of drug product recalls in 2010–2011 [13]. This delamination phenomenon has been well documented in the glass literature ever since the early 1940s when the occurrence of flakes in soda-lime glass bottles exposed to uncontrolled humidity and temperature conditions was described [11, 14].

The mechanism of glass delamination in pharmaceutical glass vials is described in Figure 8. The first stage is the formation of an altered layer caused by either extreme thermal treatments during the forming process or contact with very aggressive substances [15]. Strains are then established between the altered layer and the bulk glass having different thermal expansion coefficient. Therefore when vials are filled with the liquid preparation, this mechanically weakly linked layer is subject to a strong hydration and swelling that cause the detachment of flakes (lamellae) [16].

Many factors determine the delamination propensity of pharmaceutical glasses. A major one is the presence or absence of the surface treatments described in Section 7 (ammonium sulfur treatment, siliconization) or special coatings, which are purposely intended to produce a deep modification of the outmost surface layers.

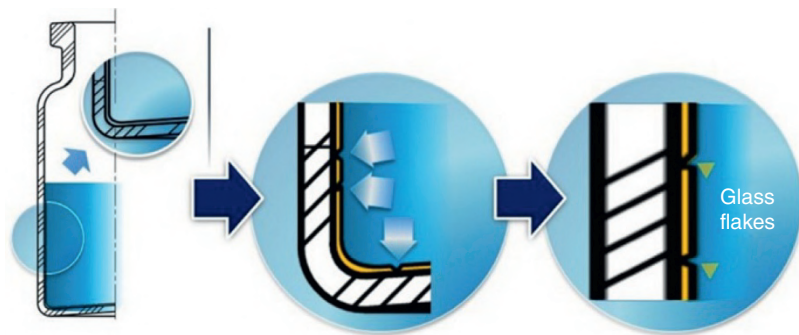


Figure 8 Mechanism of glass delamination in pharmaceutical glass vials. Inset: altered layer on the glass surface, which may detach as a flake.

The type of glass used, (e.g. CTE 33, CTE 51) or other factors such as the B_2O_3 content, in combination with the drug may play an important role on the final container delamination propensity. The nature and the pH of filling media, the presence of organic acids, and the formulation of the buffer system can trigger an extensive alteration of the glass surface together with the washing and depyrogenation process, the sterilization operations, and the storage conditions.

Reducing the risk of delamination is therefore not a simple exercise, as one has to consider and keep under control all the production stages, starting from the choice of the most appropriate glass type as a function of the chemistry between glass and the pharmaceutical solution, the optimization of the glass container forming process, the subsequent filling operations, and the shelf life of the product. These checks should be made in accordance with the European Pharmacopoeia, which, for instance, states that “Accelerated degradation testing can be used as a predictive tool to select the most appropriate container for the intended preparation, but the full compatibility of the active substance with the glass leachate can only be assessed by a stability test under normal conditions of use.”

6.3 Tungsten

Recent studies have shown that soluble tungsten polyanions may cause the precipitation and/or the aggregation of biomolecules such as monoclonal antibodies to form visible particles. It has also been reported that exposure of proteins to increasing concentrations of tungsten polyanions in acidic pH strongly favors aggregation and may induce reduced activity and increased immunogenicity.

Although borosilicate glass containers do not contain tungsten, a tungsten-containing pin is kept in contact with the glass tip during the cone formation of glass syringes to form the bore where the needle will be accommodated in a later stage. The use of pins at elevated temperatures favors the formation of tungsten oxides (WO_3 and WO_4), which evaporate and interact with the outmost glass surface of the funnel. They then form soluble sodium tungstate polyanions, which are easily extractable. When present, sodium tungstate can be observed as white spots in scanning electron micrographs of the inner surface of the funnel (Figure 9). Hence, the maximum permissible concentration of tungsten that is deemed not to cause any adverse effect to

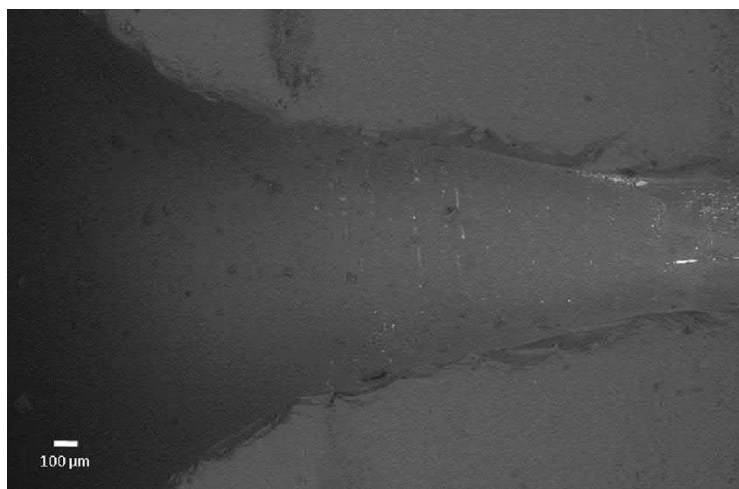


Figure 9 Tungsten residues of the inner surface of a syringe cone as seen as bright zones in a scanning electron micrograph compositional image (92× magnification). Courtesy Giovanni Stevanato Laboratory (Ca' Foscari University of Venice, Italy).

biopharmaceuticals, around 500 mg/l, can be respected only through a very controlled and precise forming process of the syringe cone.

6.4 Particle Release

The European, US, and Japanese pharmacopeias have set limits and provide techniques for detecting and quantifying visible and subvisible particulate in parenteral solutions that might compromise the safety of the patient. Glass containers must actually be “practically free” from visible particles [17]. These regulations provide limits for *extrinsic* particles, such as hair and dust, in terms of a maximum allowed number depending on particle size. In particular, limits set for the number of subvisible particles are 6000 for particles greater than 10 μm and 600 for particles greater than 25 μm . The regulations set also limits for *intrinsic* and *inherent* particulates. Intrinsic particles originate from the production process. They are usually composed of silicone oil, stainless steel, or glass. Inherent particles, on the other hand, are product related – an example is given by protein particles in biotechnological formulations. Current processes have drastically reduced the size and occurrence of particles, and the latest technological advances have significantly improved their detection and quantification. The three types of particulate are carefully monitored in glass primary packaging.

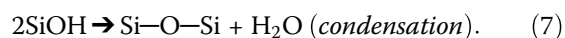
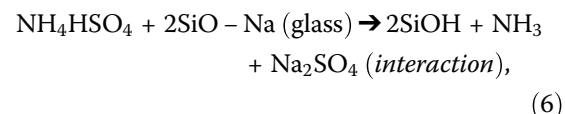
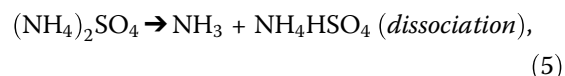
In particular, silicone oil subvisible particles may migrate from a siliconized container (typically prefilled syringes) to the drug solution. Also, the movement of the stopper during the injection may ease the migration of silicone oil into the drug. This concern can become serious when the number of dispersed particles exceeds the limits set by the pharmacopeia. The presence of silicone oil may also accelerate aggregation in proteins and, when injected, aggregates elicit immunogenic responses [18].

7 Internal/External Treatments for Chemical/Mechanical Resistance

A large array of solutions is available to address the aforementioned corrosion and interaction issues. These solutions come in the form of internal or external treatments, which can be applied to glass containers to improve their resistance. Some of them have become standard in the manufacturing practice, whereas others are still an area of active research. The three most common treatments are ammonium sulfate treatment, siliconization, and glass strengthening.

7.1 Ammonium Sulfate

The ammonium sulfate treatment was originally designed to improve the chemical durability of the inner surface of type III glass containers. The process is carried out on molded soda-lime containers before entrance into the annealing lehr. The ammonium sulfate solution is sprayed in-line on the highly reactive surface of the virgin vial. The reaction occurs according to the following scheme:



This treatment extracts alkaline and earth alkaline elements from the surface and generates a bloom made of alkali sulfate salts that confer an opalescent aspect to the containers. This layer is easily removed in a subsequent washing step that leaves behind a silica-enriched surface for a depth that depends on the penetration of the treatment, generally down to 0.5 μm . As a result, the containers become classified as type II because they have an excellent chemical durability, comparable with that of type I, but restricted to a thickness of a few hundred nanometers below the surface. Alternative treatments with 1-2-difluoroethane or gaseous sulfuric acid are occasionally used for molded vials at the same purpose.

The same treatment can be applied to type I glass containers before the annealing lehr and specifically on containers filled with drugs or solvents particularly sensitive to pH shifts. The advantages of the sulfur treatment are a reduction of alkali release, an easier compliance with pharmacopeia and an easy integrability of the process in the production lines. As for its disadvantages, they are of course an increased cost due to the additional processing step but especially the creation of surface inhomogeneities, which increase dramatically the risk of glass delamination when the thickness of the modified surface layer increases.

7.2 Siliconization

Prefilled syringes and cartridges operate through a plunger that moves along the inner surface of the glass barrel. To ensure the smooth movement of the plunger, silicone oil is commonly employed as a lubricant. In Section 6.3, however, there is evidence that proteins may form aggregates by interactions with it. Nonetheless, a lubricant is necessary to guarantee suitable values of break-loose and glide forces and enables a correct fluid

flow during injections. Internal treatments have therefore been developed to deposit a layer of silicone oil on the glass surface so that detachment of silicone particles can be reduced and the mechanical gliding properties can be assured [19]. The layer of silicone oil is characterized by two main parameters: the quantity of silicone oil applied to the container barrel and its distribution. An excess of silicone oil may slough off from the barrel and generate particles, so care has to be taken to deposit only the proper amount. Moreover, the silicone oil should be applied homogeneously throughout the container internal surface, so the degree of lubrication is constant along the plunger path.

Two main methods are currently employed to perform siliconization of pharmaceutical glass containers. In *spray-on* siliconization, the silicone oil is sprayed from a moving nozzle along the container barrel. The movement of the nozzle and the quantity of silicone that is sprayed have to be carefully controlled to achieve uniform distribution. In *baked-on* siliconization, a silicone oil emulsion is first sprayed on the container inner surface and then baked at high temperature. In the literature, baking temperatures from 100 to 320 °C have been reported, depending on the desired characteristics of the silicone layer that forms and on the silicone oil composition. A thin layer of silicone oil directly on the glass becomes partially bonded to the surface during the baking stage. At the end of the process, the combination of bonds to the surface and polymerization contributes to the adhesion of silicone oil to the glass barrel. Baked-on siliconization leads to decreased migration of silicone oil into the drug product without seriously compromising the functionality of the lubrication. However, a careful selection of the operating temperatures and times has to be performed as the silicone bulk properties could change through thermal decomposition during the baking phase. Recently, novel coating methods utilizing cross-linked silicone have been developed to reduce further silicone sloughing off from the container barrel. Silicone oil-free systems such as low-friction plungers and stoppers that could enable suitable gliding performances in silicone-free glass containers are now under investigation.

7.3 Glass Strengthening

Because most of the strength-limiting defects in glass articles are created by mechanical contact or localized thermal shock, attention has to be focused on the manufacturing and transportation processes. For pharmaceutical applications, the use of an appropriate glass-tubing converting process can limit the presence of surface

flaws in the glass, allowing the production of glass containers with increased mechanical strength.

If a particular mechanical resistance of the glass container is requested, a *chemical* strengthening processes (ion exchange) can be applied. Since the process is described in Chapter 5.12, it will suffice here to state that the glass container is submerged into a molten potassium nitrate salt. An ion exchange process takes place, in which sodium ions of the glass are replaced by potassium ions from the bath. As the potassium ions are bigger than the sodium ones, their presence in the surface creates a state of compression. The depth profile of the potassium layer is tuned to the bath temperature and time. Suitable depths of the potassium layer can produce compressive surface states that limit the effects of surface defects, considerably increasing the mechanical performances.

8 Perspectives

Even though glass has been used for a long time to store pharmaceuticals, advances in glass composition, container performance, and glass treatments are still important areas of research. As a matter of fact, the synergy between glass manufactures and pharmaceutical companies is getting stronger every day. An example of this is given by novel therapies for which there is a need for containers that are able to protect and store more complex and aggressive formulations throughout the product shelf life. An increased level of flexibility is thus requested by the market, with the constraint of satisfying all the requirements that guarantee the quality of the product. One can achieve this objective by improving manufacturing process, applying new treatments, and using new glasses compositions. For example, coatings could be developed to improve the adhesion of silicone oil on the inner surface of glass containers.

There is a general worldwide action for the reduction of the costs associated to healthcare. As a consequence, self-administration of drugs is becoming more and more common. A transition from infusion to subcutaneous injections is progressively taking place for diseases such as diabetes and cancer treatments. This trend is driving the development of new container formats, whose shapes and volumes are determined by the new therapies and drugs. The very concept of glass for pharmaceutical packaging is evolving: from a mere container to store the product, glass is becoming a fundamental part of medical delivery devices. In these systems, the packaging and the drug are fully integrated to provide the maximum efficacy of the therapy. To be realized, this transition must be performed through a rational approach. The

interactions between the glass and the therapeutic formulation have to be further deeply investigated on a scientific basis to characterize the occurring phenomena and understand their implications on drug stability. Solid theoretical and statistical grounds should guide the optimization of the manufacturing process, so the quality of the final product is pursued from the design stage to the final use by the patient.

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7.8

Oxynitride Glasses

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1 Introduction

In oxynitride glasses, oxygen atoms are partially replaced by nitrogens in the silicate or aluminosilicate network [1–4]. Oxynitride glasses have been synthesized with different modifying cations such as Li [5], the alkaline earths (Mg, Ca, Ba, Sr) [1, 6, 7] or Y [1–4, 8], and the rare-earth lanthanides (Ln) [3, 4, 9] as well as mixed modifiers [10].

Following some early work on solubility of nitrogen in soda-lime-silica glasses [11], it was discovered that silicon-nitride-based ceramics contained oxynitride glass phases in grain boundaries when oxide additives were used for liquid-phase sintering of the product [12]. The main oxide additives used were yttria and alumina. They react with the silicon nitride and silica on its particle surfaces to form a Y–Si–Al–O–N liquid phase at high temperatures, which subsequently cools to form intergranular glass films. Interest was then further stimulated, particularly in Y-modified oxynitride glasses, because the chemistry and volume fraction of the intergranular glass phases determined the properties of the material, particularly their ambient and high-temperature mechanical behavior.

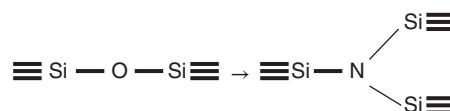
Further studies of the formation, structure, and properties of bulk oxynitride glasses showed them to have higher elastic modulus, hardness, glass-transition temperature, and viscosity than their oxide glass counterparts as a result of extra cross-linking of the glass network when nitrogen substitutes for oxygen [1–4, 8–10]. Thus, oxynitride glasses became one additional type to the range of specialty or “new” glasses with novel functions which

have potential for use in modern industrial sectors such as optoelectronics, microelectronics, communications technologies, biomedical devices, and niche areas of the automotive and architectural sectors.

In this chapter, we will first describe why so much nitrogen can dissolve and how the complex compositions of these materials are conveniently pictured in terms of Jänecke’s prism. The peculiar structural features and stronger atomic bonding of oxynitride glasses will then be discussed before the composition dependence of their physical properties is presented. Finally, glass–ceramics, phosphate glasses, and ways to make preparation of these materials easier are presented.

2 Solubility of Nitrogen in Glasses

The physical solubility of nitrogen in soda-lime-silica glasses is extremely low if the gas is bubbled through the melt (Chapter 5.5, [11]). If ammonia gas is bubbled instead for five hours at a temperature of 1400 °C, however, the chemical solubility of nitrogen in the glass reaches 0.33 wt %. From this value some 10⁵ times higher than that for physical solubility, it was proposed that nitrogen substitutes for oxygen in the SiO₄ tetrahedra within the silicate network when conditions are reducing [11]. This substitution leads to a higher than average coordination of nonmetal atoms as in:



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This results in increased cross-linking and, hence, a more rigid glass network.

A further study [13] found that, by heating in ammonia, 3 wt % N could be incorporated into the structure of porous borosilicate glasses, used as high-energy lamp envelopes, which resulted in increases in annealing temperature, indentation hardness, and electrical resistivity, and a significant decrease in thermal expansion coefficient. Devitrification of these glasses can be induced electrolytically as a result of buildup of alkali ions in the cathode region caused by their migration under the influence of the electric field. The presence of nitrogen had the interesting feature of inhibiting the transformation, an effect attributed to the increased viscosity caused by the existence of (=NH) and (=N—) groups in the structure.

An investigation of the solubility of nitrogen in CaO–SiO₂–Al₂O₃ metallurgical slags [14] found that, from 0.25 to 2.5 wt %, N is dissolved into the melt after 24 hours in a 0.1 MPa nitrogen atmosphere. By contrast, when Si₃N₄ is added to the melt, under the same conditions, 4 wt % nitrogen is incorporated much more rapidly. Hence, it was concluded that most silicate melts are not significantly reducing enough to dissolve gaseous N₂ or NH₃ so that it is necessary to dissolve instead nitrogen from nitrides such as Si₃N₄.

Since the early days of the development of silicon-nitride-based ceramics [12], the impetus for studying bulk oxynitride glasses has come from a growing desire to understand the nature of the intergranular glass phases. Typically, the preparation of these glasses [1–4] involves wet-ball milling of appropriate powders – silica, alumina, the modifying oxide plus silicon nitride or aluminum nitride – in isopropyl alcohol with sialon milling media, followed by evaporation of the alcohol. Batches of up to 50–60 g are melted in boron-nitride-lined graphite crucibles under a 0.1 MPa nitrogen pressure at 1650–1750 °C for 1 h, after which the melt is poured into a preheated (~850 °C) graphite mold. The glass is annealed close to its glass-transition temperature (T_g) for one hour to remove stresses and then slowly cooled. In accordance with the tight nature of the bonds formed by nitrogen in the material, weight losses during melting are usually less than 1%.

3 Glass Formation in M–Si–Al–O–N Systems and Its Representation

Convenient methods of representing both Si–Al–O–N and M–Si–Al–O–N systems involve the concept of reciprocal salt pairs. The four-component Si–Al–O–N system is a square plane which has, as components, the

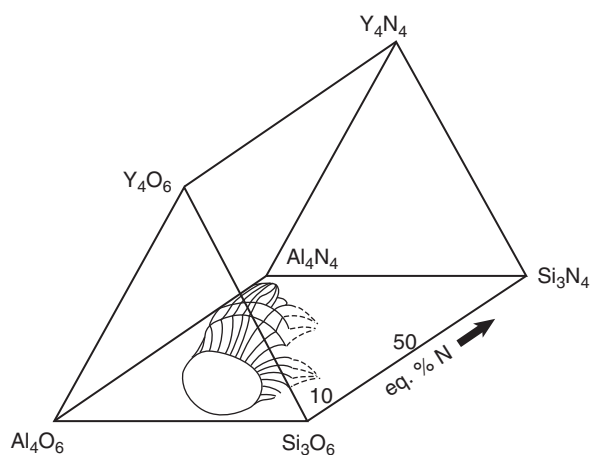


Figure 1 Jänecke's triangular prism for the Y–Si–Al–O–N system showing the complete glass-forming region for melts quenched from 1700 °C. Source: After Ref. [1].

oxides and nitrides of silicon and aluminum. The introduction of a further cation gives a five-component system represented by the so-called Jänecke's triangular prism shown in Figure 1 for the Y–Si–Al–O–N system, in which the boundaries of the complete glass-forming region are outlined [1].

As is usual in these systems, the concentrations of all components will be expressed in equivalents instead of atoms or gram-atoms. One equivalent of any element always reacts with one equivalent of any other element or species. If the top right-hand corner of the basal square represents one mole of Si₃N₄, then moving from right to left, 3 Si⁴⁺ are gradually replaced by 4 Al³⁺ and, from top to bottom, 4 N^{3–} are replaced by 6 O^{2–}, so that the corners of the square are Si₃N₄, Si₃O₆, Al₄O₆, and Al₄N₄. Any point on the square represents a combination of 12 positive and 12 negative valence units.

When moving into the prism, the third modifying “cation” (M = Y, Mg, RE, etc.) also needs to be taken into account. Any point in the prism represents a combination of 12 positive and 12 negative valence units. For a system containing three types of cations, A, B, and C with valences of v_A , v_B , and v_C , respectively, then:

Equivalent concentration of A

$$= (v_A [A]) / (v_A [A] + v_B [B] + v_C [C]), \quad (1)$$

Equivalent concentration of B

$$= (v_B [B]) / (v_A [A] + v_B [B] + v_C [C]), \quad (2)$$

Equivalent concentration of C

$$= (v_C [C]) / (v_A [A] + v_B [B] + v_C [C]), \quad (3)$$

where [A], [B], and [C] are the atomic concentrations of A, B, and C, respectively, in this case, Si^{IV}, Al^{III}, and Y^{III}.

If the system also contains two types of anions, D and E with valences ν_D and ν_E , respectively, then:

$$\text{Equivalent concentration of D} = (\nu_D [D]) / (\nu_D [D] + \nu_E), \quad (4)$$

$$\text{Equivalent concentration of E} = (\nu_E) / (\nu_D [D] + \nu_E), \quad (5)$$

where [D] and [E] are the atomic concentrations of D and E, i.e. O^{II} , N^{III} , respectively. The concentrations can then be expressed as equivalent percentages (eq. %). Any vertical plane within the prism has a constant nitrogen: oxygen ratio.

The limits of the metal aluminosilicate glass regions are plotted on the oxide face of the prism. The glass-forming region is seen to expand initially as nitrogen is introduced and then diminishes above approximately 10 eq. % N until the solubility limit of nitrogen is exceeded. Depending on the particular network-modifying cation, up to 25–30 eq. % N can be introduced into the glass.

In M–Si–O–N systems, much smaller glass-forming regions are observed (Figure 1). This feature confirms the ability of Al_2O_3 to extend the range of glass formation in both silicate and oxynitride systems. The miscibility gap in various silicate binary systems (Chapter 5.2) expands to a small extent into the equivalent M–Si–O–N system with consequent phase separation in some low-alumina glasses.

4 Structure of Oxynitride Glasses

4.1 Si–N Bonding

Early analyses of oxynitride glasses by IR spectroscopy confirmed the formation of Si–N bonds in the atomic network which, by substitution for oxygen, produces a more tightly and highly linked structure. Oxygen can coordinate with up to two Si atoms in the glass network bridging between two SiO_4 tetrahedra (Figure 2a). Nitrogen, in contrast, may be coordinated with up to three Si atoms [15] or alternatively bond with two SiO_4 units and a network-modifying cation such as Mg^{2+} or Y^{3+} (Figure 2b and c, respectively).

With ^{29}Si MAS-NMR spectroscopy it has been shown that the oxynitride network contains SiO_4 , SiO_3N (and possibly SiO_2N_2) tetrahedral structural groups [4, 16]. The $[SiO_3N]^{5-}$ group requires the presence of an extra positive charge locally to balance the extra negative charge from the N^{3-} anion. The situation is, therefore, very similar to that of an $[AlO_4]^{5-}$ tetrahedron within the glass network, which also requires an extra positive charge to make it isoelectronic with the $[SiO_4]^{4-}$ tetrahedron. For this reason, oxynitride glasses containing SiO_3N groups can

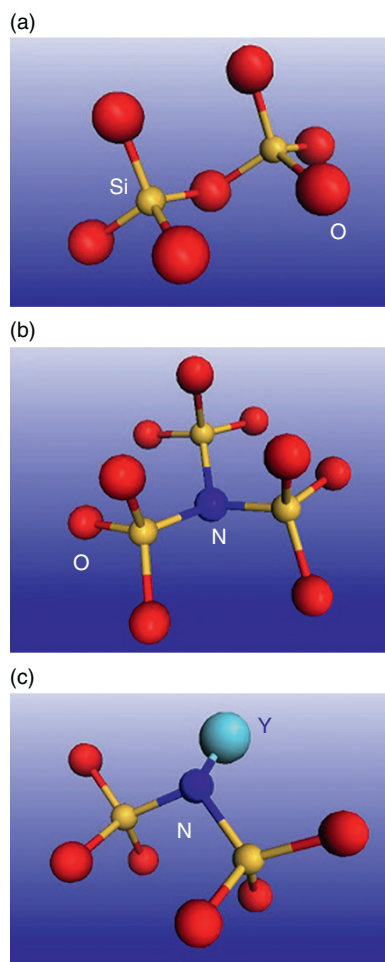


Figure 2 Bridging of SiO_4 tetrahedra. (a) Via a bridging oxygen connecting two SiO_4 units in silicate glasses; (b) via a bridging nitrogen connecting three SiO_4 units in oxynitride glasses; (c) or via a bridging nitrogen connecting two SiO_4 units and a network-modifying cation such as Y^{3+} . Source: After Ref. [4].

accommodate more modifiers in “charge compensating” sites than the equivalent oxide glasses without creating non-bridging oxygen (NBO) species.

Whereas strength is greater for the Si–O bond ($U_{Si-O} = 800$ kJ/mol) than for the Si–N bond ($U_{Si-N} = 437$ kJ/mol), calculations show that the latter is more resistant to bending [4]. Along with the increased coordination with Si, the effect is to increase the rigidity of the network because bonding is much more covalent for Si–N than for Si–O so that bending is more difficult for Si–N–Si than for Si–O–Si linkages.

4.2 Aluminum Incorporation

In oxynitride aluminosilicate-type glasses, Al (as well as Si) can be in fourfold coordination with oxygen and so act as a network former [2, 4] although the Al–O network

bond is somewhat weaker (and less covalent) than the Si–O bond. The difference in charge between Al^{3+} and Si^{4+} also requires the presence of an additional cation locally for local charge balance. Thus, Y^{3+} and Mg^{2+} would serve to balance the charges of three and two AlO_4 tetrahedra, respectively. As a modifier, yttrium has an affinity to bond with oxygen, coordinating with five or so oxygens based on results for yttrium aluminosilicate glasses [4]. For oxide glasses with a considerable ionic bond character, some general insights into the relative strengths of various M–O bonds (M = cation) can be gained from Coulombic interactions between a cation and an anion through cation field strength ($\text{CFS} = v/r^2$, where v is valency and r ionic radius). This picture, however, becomes more complicated with the introduction of strong covalent bonds (Si–N or M–N) in oxynitride glasses. Although the Y–O bond is weaker than the oxygen bond with either Si or Al, its coordination with multiple oxygens and the associated high CFS indicate that Y can improve the strength of the glass network.

4.3 Si–N vs. Al–N Bonding

For glasses with nitrogen contents up to about 20 eq. % N, MAS-NMR, FTIR, and Raman-spectroscopy studies have indicated that Si–N is preferred to Al–N bonding [9, 16]. Thus, it is possible to estimate the average number of nitrogens preferentially bonded to each silicon, i.e. x in each $\text{SiO}_{(4-x)}\text{N}_x$ tetrahedron within the glass network. For most glasses this number of nitrogens per tetrahedron varies as a function of nitrogen content without exceeding 1 until a nitrogen content of 15 eq. % is reached (Figure 3).

For a glass with a composition of 37Y : 42Si : 21Al ratio, i.e. with a higher Al : Si ratio, more than one nitrogen is bonded to a given silicon if the nitrogen content exceeds about 10 eq. %. For another glass with a composition of 21Y : 48Si : 31Al containing about 10 eq. % N, MAS-NMR data [6] indicate that one nitrogen is bonded to each silicon, which is in reasonably good agreement with the calculated value of 0.8. Accordingly, a simple calculation of the average number of nitrogens per silicon gives a reasonable estimate of the anion environment of silicons.

Virtually all Al-containing oxynitride glasses studied in detail have sufficient modifier cations to charge balance aluminum in fourfold coordination. However, the Al coordination with oxygen changes from four to five and sixfold as the Al : Si ratio increases in Y–SiAlON glasses with fixed Y and N contents [2, 17]. Whereas more Al–O–Si linkages are formed by displacement of Si–O–Si linkages, little change in the number of NBOs or in the degree of network cross-linking occurs. However, more five and sixfold coordinated Al atoms are observed when the Al : Y ratio decreases in glasses with fixed Si and N contents, and the number of NBOs actually increases

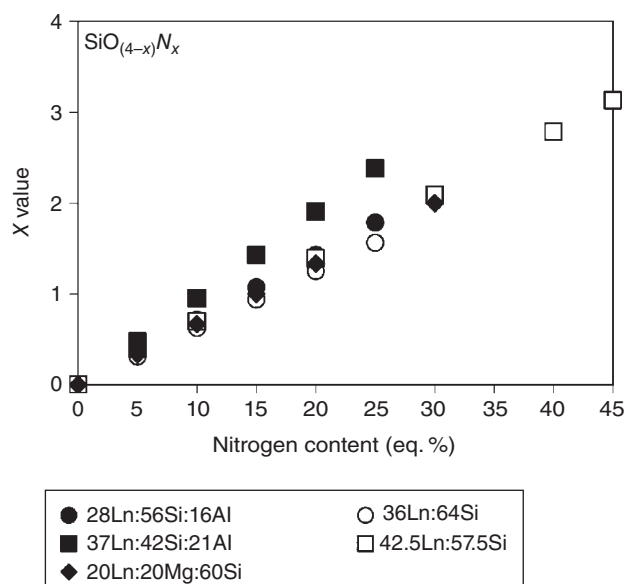


Figure 3 Average number of nitrogen atoms bonded to each silicon as a function of nitrogen content for glasses with different cation ratios (compositions expressed in eq. %). Ln represents a lanthanide (La, Nd, Sm, Gd, Yb, Er, Lu) or yttrium. Source: After Ref. [9].

because of a decrease in Si–O–Al linkages [4, 17]. The chain-like or sheet-like structures formed from $\text{Si}(\text{O},\text{N})_4$ (or AlO_4) tetrahedra are also increasingly cross-linked by Al linkages to oxygen at the tetrahedron corners as the Al content increases.

Raman spectroscopy [4] provides insights into the number of bridging oxygens (BOs) (or anions) associated with a Si-based tetrahedron, which are denoted by Q^n values, from which the relative percentages of BO and NBOs present in the glass may be obtained (Chapter 2.3). Results on the effects of nitrogen content in an Er–Si–Al–O–N glass show that a portion of each tetrahedron with only three BOs is converted to a tetrahedron with four bridges (i.e. O and N) with increasing nitrogen content. These results imply that nitrogen is incorporated into what was a non-bridging site (similar to that shown in Figure 2c). Other Raman studies [4] for oxide and oxynitride glasses with cation compositions of 55Si : 20Ln : 25Al and 45Si : 30Ln : 25Al (Ln = rare-earth lanthanide) indicate there is a shift to a greater number of Si tetrahedron bridges (i.e. an increased population of higher Q^n values) as the ratio of Si to Ln increases. This trend indicates that Si–O–Si bridges are promoted at the expense of Si–NBO–Ln linkages when Si replaces Ln, resulting in an overall increase in network connectivity. In both these oxide and oxynitride series, the number of Si tetrahedron bridges tends to increase as the size of the Ln cation decreases (as CFS of Ln increases), thus promoting greater network connectivity.

4.4 Vibrational Density of States

The substitution of N for O implies changes in the vibrational density of states $g(\omega)$ and, therefore, in the low-temperature isobaric heat capacity, C_p , which is a sensitive function of short- and medium-range order at low temperatures (<200 K). The effect of the substitution of nitrogen for oxygen on the heat capacity and vibrational entropy of three Y–Si–Al–O–N glasses with increasing N contents was investigated from 10 to 300 K [18]. The partial molar heat capacity and entropy of Si_3N_4 calculated from these and previous measurements indicate stronger average bonding than for SiO_2 units. The values derived for Y_2O_3 are consistent with both the network-modifying role of Y^{3+} and its role as a charge-compensating ion for $[\text{AlO}_4]^{5-}$ tetrahedra. These effects, along with previous elastic studies, represent the calorimetric measure of the increased rigidity and network cross-linking induced by the substitution of nitrogen for oxygen.

Inversion of the low-temperature C_p data [18] allowed the low-frequency part of the density of states to be determined. Of particular interest is the so-called boson peak, which represents either excess modes below 100 cm^{-1} compared with the $g(\omega) \propto \omega^2$ law or excess heat capacity below $\sim 50\text{ K}$ with respect to the T^3 limiting law of the Debye model. Part of the low-frequency excitations originates in the libration of a limited number of rigid TO_4 tetrahedra ($\text{T} = \text{Si}, \text{Al}$) around corner-sharing oxygens. It was observed that substitution of N for O, which enhances network cross-linking, causes a decrease in intensity of the boson peak which suggests a reduction in the librational motions of the TO_4 tetrahedra, consistent with an increased rigidity of the glass network.

In summary, the glass network in oxynitride glasses comprises $\text{SiO}_{(4-x)}\text{N}_x$ tetrahedra, with average x values controlled by N:Si ratios, which are bridged either by bi-coordinate O–T or tri-coordinate N–T linkages, and

also by AlO_4 tetrahedra which are mainly bridged by bi-coordinate O–T linkages. It is now appropriate to look at the effects of nitrogen substitution for oxygen on glass properties to determine how they are affected by replacement of bi-coordinate O–T by tri-coordinate N–T linkages and whether the effects depend or not on the nature of the modifier if the overall cation composition is kept constant.

5 Effects of Composition on Properties

5.1 General Features

As with all types of glasses, the properties of oxynitrides crucially depend on chemistry and, especially in this case, on nitrogen concentration. Early work on the correlations between nitrogen incorporation into oxynitride glasses and changes in their mechanical, elastic, and thermal properties suggested that the observed enhancement of these properties was due to increases in nitrogen content [8]. However, no account was taken of changes in Si : Al ratio or the modifying cation concentration and so changes in properties could not be attributed solely to nitrogen incorporation.

The first systematic studies on the effect of substituting oxygen by nitrogen in oxynitride glasses with constant cation compositions showed that for all Mg-, Ca-, Y-, and Nd–Si–Al–O–N glasses, increases in nitrogen did indeed result in increases in a range of mechanical, elastic, and thermal properties [1]. Further studies have investigated the effects of changes in cation ratios, keeping O : N ratio constant [2–4].

When cation ratios (M : Si : Al) are kept constant, linear correlations are typically observed between nitrogen content and various mechanical, elastic, and thermal properties [1] as summarized in Table 1 for

Table 1 Properties of oxynitride glasses.

Glass composition (eq. %)	28Y : 56Si : 16Al 0 N	28Y : 56Si : 16Al 17 N	28Er : 56Si : 16Al 17 N	35Y : 45Si : 20Al 17 N
Property				
Density (g cm^{-3})	3.59	3.78	5.05	3.97
Molar volume (cm^3/mol)	7.50	7.35	7.41	7.41
Fractional glass compactness	0.420	0.429	0.424	0.590
Young's modulus (GPa)	112 ± 2	149 ± 2	147 ± 2	148 ± 2
Microhardness (GPa)	8.8 ± 0.2	10.2 ± 0.2	10.5 ± 0.2	9.2 ± 0.2
Glass-transition temperature ($^{\circ}\text{C}$)	940 ± 2	985 ± 2	990 ± 2	940 ± 2
Coefficient of thermal expansion (CTE) (10^{-6} K^{-1})	6.6 ± 0.1	5.7 ± 0.1	6.3 ± 0.1	7.4 ± 0.1
Viscosity ($\text{Pa}\cdot\text{s}$) at $\sim 930\text{ }^{\circ}\text{C}$	10^{11}	10^{13}	$10^{13.5}$	$10^{12.5}$

28Y : 56Si : 16Al glasses either with 0 and 17 eq. % N or when 28 eq. % Y is replaced by 28 eq. % Er, as well as for 35Y : 45Si : 20Al : 83O : 17 N glasses.

5.2 Mechanical and Elastic Properties

When cation ratios (M : Si : Al) are kept constant, linear correlations are observed between nitrogen content and Young's modulus or hardness [1] (Figure 4). For a 28Y : 56Si : 16Al glass, Young's modulus increases by some 35% from 112 GPa at 0 eq. % N to 149 GPa at 17 eq. % N (Table 1). A detailed analysis of 28(Mg + Y) : 56Si : 16Al glasses showed that the slopes of plots of Young's modulus vs. nitrogen content are the same for each of three different modifier compositions used: 28 Mg : 0Y; 14 Mg : 14Y; 0 Mg : 28Y [10]. For the Mg-modified 28 Mg : 56Si : 16Al glass, Young's modulus increases by 17% as 15 eq. % N is substituted for oxygen.

For other elastic modulus and microhardness data, most reports show also good linear relationships between property values and nitrogen content with correlation coefficients generally of the order of 0.99. For elastic modulus, gradients of the plots are in the range 0.8–1.8 GPa (eq. % N)⁻¹. Thus, the substitution of 20 eq. % N for oxygen in these glasses would be expected to increase Young's modulus by values between 16 and 36 GPa. For microhardness, the gradients lie in the range 0.07–0.13 GPa (eq. % N)⁻¹, most gradients being close to 0.1 GPa (eq. % N)⁻¹ so that substitution of 20 eq. % N for oxygen would increase the microhardness of the glass by ~2 GPa.

When the Si and N contents are fixed, the values of E increase when Al is replaced by Y, such that increases

in the Y : Al ratio have the same effect on E as increasing N content.

For rare-earth lanthanide (Ln)–Si–Al oxynitride glasses, Young's modulus increases with the cationic field strength (decrease in ionic radius), which is attributed to the increasing compactness of the glass network.

Oxynitride glasses provide a good illustration of the impact of the degree of cross-linking of the glass network on the elastic moduli. These glasses are clearly stiffer than their parent oxide glasses (with the same cation ratios). However, the values for the bonding energies do not fit with these trends: $U_{\text{O-Si-N}} (437 \text{ kJ/mol}) < U_{\text{O-Si-O}} (800 \text{ kJ/mol})$. The reason for the excellent stiffness of oxynitride glasses appears to have more to do with the 3-D bonding architecture, including the property of compactness or atomic packing density, rather than the bond strength per se.

5.3 Thermal Properties – Glass Transition Temperature, Softening Temperature, Viscosity, Thermal Expansion Coefficient

The effects of nitrogen content on glass-transition temperature (T_g) at constant cation ratios are summarized in Figure 5. As with mechanical properties, one observes excellent linear correlations between nitrogen substitution levels and glass-transition temperature. For a 28Y : 56Si : 16Al glass (Table 1), T_g , for instance, increases from 940 to 985 °C between 0 and 17 eq. % N, i.e. with a slope of ~2.7 °C (eq. % N)⁻¹. These gradients are actually in the range 2.6–4.1 °C (eq. % N)⁻¹ with most values close to 3.5 °C (eq. % N)⁻¹. Thus, for a 20 eq. % N substitution level, T_g is expected to increase by ~70 °C. Littleton and dilatometric softening temperatures also increase linearly with nitrogen content, the slopes for the latter being similar to those for T_g with values in the range 2.3–3.8 °C (eq. % N)⁻¹.

For lanthanide (Ln)–Si–Al oxynitride glasses, where the nitrogen to oxygen ratio is kept constant, the glass transition and softening temperatures tend to increase as the ionic radius of the rare-earth cation decreases, that is as cationic field strength increases [4, 9].

Oxynitride glass viscosity increases with increasing nitrogen substitution and, like glass-transition temperature and softening temperatures, varies linearly with nitrogen content as shown in Figure 6. As shown in Table 1, for a glass with composition (in eq. %) of 28Y : 56Si : 16Al, substitution of 17 eq. % N for oxygen results in an increase in viscosity of ~2 orders of magnitude.

However, there is quite a wide variation in viscosity with nitrogen content that depends on cation type and ratios. For an increase in nitrogen content from 0 to 20 eq. %, viscosity increases can vary between 2.0 and 3.6

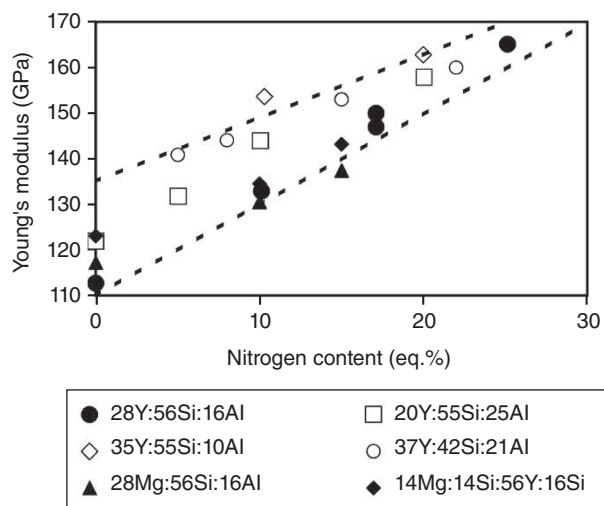


Figure 4 Linear increases of Young's modulus of oxynitride glasses with increasing nitrogen content.

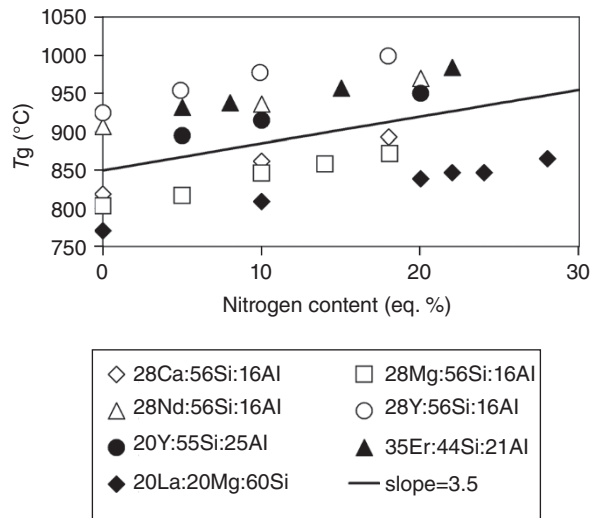


Figure 5 Glass-transition temperature (T_g) of oxynitride glasses increases linearly with increasing nitrogen content.

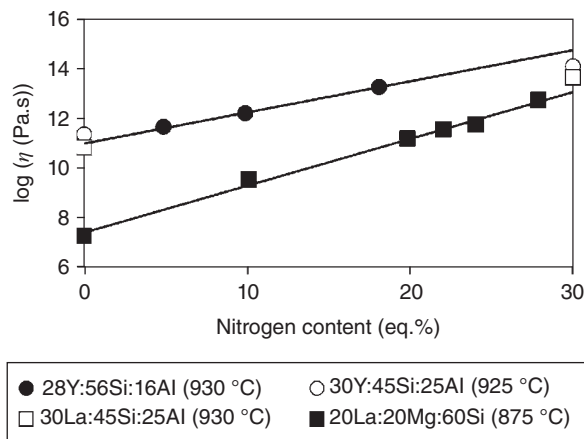


Figure 6 Effect of nitrogen content on viscosity (log scale) for oxynitride glasses with various cation compositions (in eq. %) at temperatures of 875, 925, and 930 °C. Source: After Ref. [9].

orders of magnitude. These effects are a result of the increase in the rigidity and covalence of the bonding of the network with the addition of nitrogen, which would serve to inhibit relaxation of the network as the temperature increases. On the other hand, changes in the Si, Al, and Y contents have much smaller and sometimes opposing effects on the temperature-dependent viscosity profiles. At high Al : Y ratios, when four co-ordinated Al dominates, there is an enhancement of the cross-linking of the glass network, so reducing the number of non-bridging anions. At lower Al : Y ratios, there is a decrease in network compactness due to an increase in five- or six-co-ordinated Al atoms.

In rare-earth Ln–SiAlON glasses, the temperature-dependent viscosity shifts to higher temperatures as the

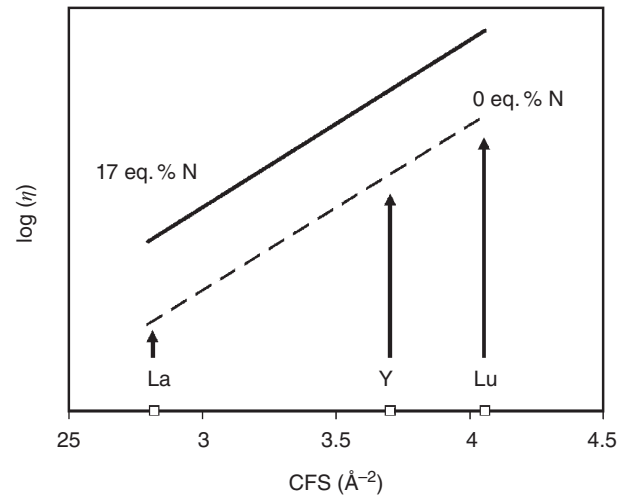


Figure 7 Schematic plot showing the combined effects of cation field strength and nitrogen content on the viscosity of Ln–Si–Al–O–N glasses at a fixed temperature.

lanthanide ion size decreases [9]. It is thought that these ions affect the molar volume in such a way that the smaller ions exert stronger bonding (i.e. higher CFS of the Ln ion) on the (Si, Al)(O, N)₄ tetrahedra and form a more compact network. In summary, glasses containing more N, less Al, and smaller Ln cations will have higher viscosities. Overall, a change of five to six orders of magnitude in viscosity can be achieved by careful modification of glass compositions as shown schematically in Figure 7. The activation energies for viscous flow increase as CFS increases so that, at any temperature, glasses with smaller cations have higher viscosities and the activation energies for viscous flow are higher, reaching values of >1300 kJ/mol for Lu–SiAlON glasses.

Although some data show negligible changes, many observers have reported decreases in coefficients of thermal expansion (CTE) with increasing nitrogen content at temperatures from just below the softening point down to ambient [4]. As shown in Table 1, for a glass with composition (in eq. %) of 28Y : 56Si : 16Al, substitution of 17 eq. % N for oxygen results in a decrease in CTE from 6.6 to $5.7 \times 10^{-6} \text{ K}^{-1}$.

When the Si and N contents are fixed, T_g values, as well as CTE, increase when Al is replaced by Y.

5.4 Fracture, Strength, Slow Crack Growth

Early results on the room-temperature flexural strengths of Li–K–Si–Al- and Y–Si–Al-oxynitride glasses indicated that there is no real effect of nitrogen content [4], but the surface conditions of the specimens were not given. Later work also reported [4] that the flexural strengths of oxide and oxynitride (17 eq. % N) glasses with

the cation composition 45Si : 20Al : 35Y in as-polished conditions are very similar. After annealing 20 °C below and above T_g , the strength of the oxynitride glass doubled and increased threefold, respectively. The oxide glass exhibited an increase of only ~50% after annealing under these same annealing conditions.

Data on fracture [4] for various oxynitride glasses indicate that the toughness increases slightly as nitrogen content increases up to ~8 eq. %. However, toughness values often change very little if at all with nitrogen content and then appear to depend more on the modifying cation and cation ratios. Thus, the compositional effects are more complex than simply determined by nitrogen content even though for some glasses the dependence on this factor appears to follow changes in the Young's moduli.

A related but quite remarkable effect is the fact that nitrogen additions clearly increase the resistance to slow-crack growth of these glasses. Three studies of Si–Y–Al glasses revealed that the addition of nitrogen shifts the range of slow-crack growth to significantly higher applied stress intensity ranges as compared to that for oxide glasses [4]. This effect can be attributed to a reduction in the fraction of threefold –Si–O ring structures when nitrogen is added, which are resistant to fracture in inert environments but fail readily in the presence of water. As compared to oxide glasses, the benefits of nitrogen-bearing glasses are that they exhibit longer lifetimes under fixed applied stress conditions and/or more limited reductions in strength when stressing rates are reduced.

5.5 Optical and Electrical Properties

Because of the higher ionic polarisability of nitrogen with respect to oxygen, the refractive index of Mg-, Ca-, Y-, and Ln–Si–Al–O–N glasses increases with increasing nitrogen at constant cation composition [1]. The modifying cation nonetheless plays a role in that the refractive index generally increases with the concentration of lanthanide cation and also with the ionic radius of the rare-earth cation [4].

When nitrogen substitutes for oxygen, IR transmission is significantly improved, whereas UV transmission is impaired because of impurities in the glass [1].

Studies of luminescence of Ce(III)–RE–Si–Al–O–N glasses revealed that 5d–4f emission shifts to longer wavelengths as the Ce ion content increases [19]. At low concentrations, Ce^{3+} displaces RE^{3+} ions (RE = Sc, Y, La, Gd) from large, more ionic sites in these glasses close to Al, yielding the short wavelength emission [4, 19].

Early studies of Y–Si–Al–O–N glasses showed increases in dc conductivity and low-temperature dielectric constants with N concentration, but these results were reported for glasses lacking systematic changes in

composition. Subsequent work [1] indicated that the dielectric constants of Mg-, Ca-, and Y–Si–Al–O–N glasses with fixed cation contents do increase with nitrogen levels.

6 Oxynitride Glass–Ceramics

Like other silicate glasses (Chapter 7.11), oxynitrides may be annealed at appropriate temperatures to form glass–ceramics. The crystalline phases formed depend on both the composition and heat treatment of the parent glass. The conventional process to produce a glass–ceramic involves two steps (Chapter 5.4): (i) a low-temperature heat treatment to induce nucleation followed by (ii) heating to a higher temperature to allow the growth of the crystalline nuclei. Usually glasses require the addition of a nucleating agent to promote the crystallization process [7] but oxynitride glasses are self-nucleating whenever the slightly reducing atmosphere used for their preparation causes the precipitation of FeSi particles on which heterogeneous nucleation then takes place.

Many studies of crystallization of oxynitride glasses have concentrated on the Y–Si–Al–O–N system. The glass–ceramic transformations in a glass of composition 28Y : 56Si : 16Al : 830 : 17 N were studied with both the “classical” two-stage glass–ceramic heat-treatment process outlined above and a differential thermal-analysis technique [20]. In the classical process, a series of heat treatments (below and above T_g) were carried out in a tube furnace to determine the optimum nucleation temperature that corresponds to the largest volume fraction of crystalline phase formed and the finest crystal size. The differential thermal analysis (DTA) method involves isothermal holds in the same temperature range as the classical method for a constant time at different nucleation temperatures, followed by heating at a constant rate up to the observation of the crystallization peak temperature. These two methods were found to be in close agreement [20]. Optimum nucleation and crystallization temperatures were determined in relation to the glass-transition temperature. The major crystalline phases present are mixtures of different forms of yttrium disilicate and silicon oxynitride. Bulk nucleation is the dominant nucleation mechanism. The activation energy for the crystallization process is 834 kJ/mol. In glasses with higher Al : Si ratios, as nitrogen content increases, gradual replacement of yttrium disilicate phase by yttrium aluminum garnet (YAG) is observed and nitrogen is mainly incorporated into Si_2N_2O .

A separate study [2] of crystallization of a glass with the 35Y : 45Si : 20Al composition containing 23 eq. % N allowed precipitation of B-phase (Y_2SiAlO_2N),

Iw-phase ($\text{Y}_2\text{Si}_3\text{Al}_2(\text{O},\text{N})_{10}$), and wollastonite (YSiO_2N) at temperatures below 1200°C whereas α -yttrium disilicate ($\text{Y}_2\text{Si}_2\text{O}_7$), apatite ($\text{Y}_2\text{Si}_3\text{O}_{12}\text{N}$), and YAG ($\text{Y}_3\text{Al}_2\text{O}_{12}$) formed at higher temperatures. At the relatively low temperatures of ~ 950 – 1100°C , the nucleation and growth of N-wollastonite (YSiO_2N) and of the intermediate phases B and Iw are kinetically favored over those of the more stable equilibrium phases YAG and $\text{Si}_2\text{N}_2\text{O}$. In the initial stages of crystallization of this glass, the creep rate is higher than for the parent glass since the residual glass following nucleation has a lower viscosity caused by a decrease in yttrium and an increase in impurity cations. After complete crystallization, however, the creep rate is very low. On a similar glass with 17 eq. % N, a double-stage glass–ceramic heat treatment (960°C for one hour and 1050°C for five hours) allowed crystal growth to form B-phase. A flexural strength of 550 MPa was measured for the glass–ceramic. This compares with many commercial glass–ceramics that have strength values in the range 120–350 MPa depending on composition and crystal morphology present.

7 Phosphorus Oxynitride Glasses

The chemical resistance, thermal, and optical properties of phosphate-based glasses (Chapter 7.9) can be improved through the introduction of nitrogen into their structure by cross-linking polymeric phosphate chains together in the glass network. As indicated by NMR analysis, nitrogen replaces oxygen in the phosphate glass network by bonding either to two phosphorus atoms (via one double bond and one single bond) or to three phosphorus atoms via three single bonds [21].

Because melts containing P_2O_5 and N are prone to decompose, processing of phosphorus oxynitride glasses is restricted to much lower temperatures ($<900^\circ\text{C}$) than for silicates. But Si-free phosphorus oxynitride glasses have been successfully produced by nitridation of alkaline or alkaline earth phosphate glass frits under anhydrous ammonia [22] or dissolution of metal nitrides into the melt. In these systems, nitridation reaches a stability limit at ~ 800 – 900°C . Above this range phosphorus is lost from the melt as a result of reduction from P^{V} to P^{III} and subsequent volatilization and reaction with atmospheric moisture to form phosphine, PH_3 .

Properties such as glass-transition temperature, dilatometric softening point, refractive index, viscosity, microhardness, and chemical durability all increase with increasing nitrogen content whereas thermal expansion coefficient decreases as in silicate-based oxynitride glasses [21, 22].

8 Lower-Temperature Preparation Methods

One of the major disadvantages to the use of oxynitride glasses for high stiffness/high hardness applications is the fact that melting at temperatures of the order of 1650 – 1700°C are required to achieve sufficiently low viscosities for glass pouring. Increased viscosities also mean that glass forming or drawing processes must be carried out at higher temperatures than are normal for conventional glasses. However, fluorine can be successfully substituted for oxygen at the same time as nitrogen [9]. The network-terminating effect of fluorine induces significant reductions in both glass melting temperatures and T_g /dilatometric softening temperatures. Despite these decreases, elastic modulus and hardness are virtually unaffected by fluorine substitution. This latest extension of oxynitride glass development may facilitate exploitation of the excellent stiffness and hardness characteristics of these glasses, thanks to their lower processing temperatures.

9 Perspectives

Oxynitride glasses are a group of specialty glasses with superior properties to their oxide glass counterparts, one of a range of “new” glasses with novel functions that are being developed for potential technological applications. Their mechanical, rheological, and optical properties can be tailored by changes in their composition, especially nitrogen content and also various alkaline-earth or rare-earth-modifying ions.

There are still significant challenges in developing oxynitride glasses for use in optical applications. In order to develop optically transparent glasses, a more fundamental understanding of the reactions occurring during synthesis and the mechanisms involved in the formation of such glasses is required along with development of methods for eliminating impurities in the final product such as elemental silicon and silicides. However, because of their lower densities, these glasses are now being investigated as potential materials for use in more lightweight applications in modern communications equipment, in biomedical devices, and where reductions in energy usage are critical. In view of their superior durability, higher stiffness, higher hardness, higher softening points, and tailored thermal properties, oxynitride glasses may find use in various “nonoptical” applications.

These novel applications of oxynitride glasses include passive coatings on electronic substrates using their higher dielectric constants and elastic moduli to best

advantage; special windows for aerospace applications where their higher elastic moduli would allow them to remain stiff in thinner sections, thus allowing weight and energy savings; new bioactive oxynitride glasses and glass–ceramics with better load-bearing properties; glass-decoration enamels using the color effects found in Ln–Si–Al–O–N glasses; glaze systems for refractory protection taking advantage of their higher viscosities; joining of silicon nitride-based ceramics and of these ceramics to metals, where the grain boundary glasses are similar in composition to the bulk glasses; higher-temperature range glass–ceramics for structural applications where their higher refractoriness would make them more stable at higher service temperatures.

So far, oxynitride glasses have not found any major commercial uses. The gains in properties are not significant enough to compensate for the increased production costs arising from the more difficult manufacturing processes involved, which require controlled nitrogen atmospheres at temperatures of 1650–1700 °C. In order to make a significant breakthrough in terms of commercial glass products, the major challenge that needs to be addressed is the development of more cost-efficient and up-scalable synthesis methods. Some companies have confidential ongoing programmes to investigate these possibilities.

One solution that would allow melting temperatures to be reduced is the substitution of oxygen by both fluorine and nitrogen. The higher elastic modulus and hardness conferred by nitrogen is maintained which might allow exploitation in some of the specialist applications outlined above.

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7.9

Phosphate Glasses

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1 Introduction

Phosphorus was an unintended by-product of alchemical speculations. Searching for the philosophical stone (Chapter 10.10) in human urine, Hennig Brand (seventeenth century) ended up toward 1669 isolating the new element from the *microcosmic* salt $[\text{Na}(\text{NH}_4)\text{HPO}_4]$ and termed it *light bearer* (*phosphoros*, in Greek, the name also given to the planet Venus) because of the glow caused by its slow, spontaneous combustion. Thanks to this most unusual property, phosphorus aroused considerable attention before giving progressively rise to a rich chemistry. Polyphosphates were, for instance, first synthesized by Jacob Berzelius (1779–1849) in 1816 as an ignition product of orthophosphoric acid. Phosphate glasses are a subgroup of polyphosphates. One of them is the well-known Graham's salt, which was produced in 1833 [1] by fusion of sodium hydrogen phosphate (NaH_2PO_4), which induces dehydration reactions yielding first $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ and then $(\text{NaPO}_3)_6$. In 1848, Fleitmann and Hennenberg then pointed out that this substance was most likely a mixture of polyphosphates with different chain lengths.

Because of the limitations of purification methods, however, a century elapsed before the structure and chemistry of these substances could be properly studied. Molecular weight separation by paper chromatography was then a key advance as particularly well illustrated by Van Wazer in his 16-part series on the structure and properties of condensed phosphates [2]. Crystallography provided in the 1940s the first insights into P–O bond distances in isolated crystals. Not surprisingly, much progress has been made since then on both

crystalline and glass phases, thanks to modern characterization methods.

Phosphate glasses were first applied to mineral analysis and water softening. Interest in optical applications was raised at the very beginning of the twentieth century but vulnerability to moisture was problematic. Very broad spectral windows from the ultraviolet (UV) to the near infrared (IR) was so much an asset, however, that water-stable compositions were devised in the 1940s [3]. Building on the work of Van Wazer and his contemporaries in the 1950s, development of solid-state lasers took place in the 1960s after it had been discovered that these glasses could take up large amounts of rare earth elements. This affinity for rare earths led them to be used also for nuclear waste containment in the 1970s (Chapter 9.11). As for the vulnerability to water, it has recently been turned into a benefit in absorbable medical devices and in controlled delivery of trace elements. Last but not least, interesting electrical properties have sparked research into the use of phosphate glasses in dielectrics, semiconductors, and fast-ion conductors.

In this chapter, the structure of phosphate glasses will first be described in terms of the speciation of PO_4 groups and the length of phosphate chains. Next, the synthesis of these glasses and the problems raised by their affinity for water and by their corrosivity will be summarized. Practical applications will then be reviewed. Their extent is not readily ascertained because the vitreous nature of products is not always indicated. The nearly a thousand patents filed since 1926 nonetheless gives an idea of their variety. Specific values of tonnage production per year are difficult to find, though several hundred thousand tonnes of calcium magnesium phosphate glass are produced as a fertilizer in Asia and South America [4]. The most conspicuous use is in optical systems, but the ability to control the exchange of ions with phosphate glasses is at the roots of less visible, but much more common

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applications. Only the main ones will be dealt with here. Many others are described in the literature [2, 5–7].

2 Structure

2.1 Phosphate Groups

Condensed phosphates consist of corner-to-corner connected tetrahedral PO_4 groups forming chains and networks (cf. [8, 9] for more detailed information). There are no edge or face connections, which would give rise to highly stressed cyclic groups. Although phosphate chains are flexible, the P–O bond length average is remarkably constant at about 1.54 Å, with internal bond angles of 110–120° and intra-tetrahedral angles of 125–155° [3, 10]. Through charge repulsion, chains of 5–10 tetrahedra are typically straight, but increase in flexibility as length increases beyond 10. The greatest degree of freedom results from bond rotation, which allows for a great variety of conformations as illustrated by the Rubik's snake toy.

The phosphate groups in a chain or network structure are described in terms of Q^n species where n indicates the number of bridging oxygens in a tetrahedron (Figure 1). With respect to silicates (Chapter 2.4), the difference is that the 5+ nominal charge of P requires an extra P–O bond, which translates into a double bond in Q^3 species only because resonances make all nonbonding P groups equivalent in the others. Among glass formers, phosphates perhaps show the closest structural similarity to organic polymers (Chapter 8.8) because of the great many different ways in which Q^n species can form a networked or cross-linked structure with chains of different lengths. This is why they have been referred to as *inorganic polymers* [11].

It is useful to distinguish these different structures with the nomenclature used by Graham for polyphosphoric acids, namely

Orthophosphoric acid	3 H_2O :1 P_2O_5	$\sim \text{H}_3\text{PO}_4$
Pyrophosphoric acid	2 H_2O :1 P_2O_5	$\sim \text{H}_4\text{P}_2\text{O}_7$
Metaphosphoric acid	1 H_2O :1 P_2O_5	$\sim \text{HPO}_3$

In terms of Q^n speciation, orthophosphates thus represent isolated Q^0 , pyrophosphates Q^1 dimers, and metaphosphates Q^2 chains, where H_2O can be replaced by

other modifier oxides, M_2O . When the ratio of modifier to P_2O_5 falls below 1 : 1, i.e. for more than 50% P_2O_5 , Q^3 cross-links begin to form and create what Kroll called in 1912 an *ultraphosphate*. Recently, glasses between pyrophosphate and orthophosphate have become known as an *invert* (Chapter 10.11), because their properties are dominated by the modifiers rather than by the glass formers. They are also referred to as *ionic polymers* as they represent effectively a series of linked anions and cations without a covalent glass network. The ratio $\text{M}_2\text{O}/\text{P}_2\text{O}_5$ is generally denoted as R . The ortho-, pyro-, and metaphosphates thus refer to R values of 3, 2, and 1, respectively. In between them, one then finds invert glasses/ionic polymers (3–2), poly-(2–1), and ultraphosphates (1–0), respectively.

Any chain must of course have two ends, such that a linear metaphosphate could only exist as an infinitely long chain. Metaphosphates have in fact cyclic structures that have been observed with up to eight units; larger cycles likely exist but have not been isolated yet. With up to 10^6 units, the effect of end groups of course becomes vanishingly small, which is why chains can generally be referred to as metaphosphates although they should really be described as polyphosphates.

As justified by Van Wazer [2], the general structure of phosphates can be described by the formula:

$$\text{M}_{nR}\text{P}_n\text{O}_{n(5+R)/2}, \quad (1)$$

where n is the number of P atoms and nR and $n(5+R)/2$ must also be integers. The special cases of zero and unity values for R thus refer to P_2O_5 and MPO, respectively. A simple relationship then yields the theoretical phosphate chain length from the ratio R as:

$$n = 2/(R - 1). \quad (2)$$

Taking $R = 1.5$ as an example, one obtains $n = 4$ and, thus, the formula $\text{M}_4\text{P}_4\text{O}_{13}$. This relationship is very useful when manufacturing phosphate glasses to achieve a particular structure even though the value obtained is an average. It refers to a distribution whose width depends on the degree of homogenization of the glass, the nature of the modifiers, and the actual water content since H_2O can be considered as a modifier oxide.

The chain length of polyphosphates changes exponentially with the modifier content when R tends to unity (Figure 2) so that n , for instance, increases from 100 to

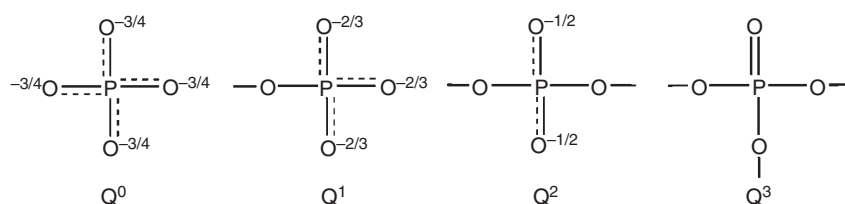


Figure 1 The Q^n speciation of phosphate groups. Resonances indicated by dotted lines, making nonbonding P groups equivalent in all but Q^3 species. Q^0 species are actually relatively unusual.

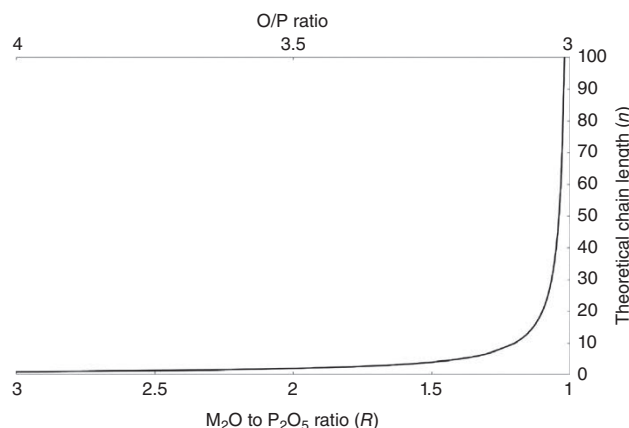


Figure 2 Exponential increase in the theoretical chain length of phosphates (n) as a result of changes in the modifier to former ratio (R) according to Eq. (2). Equivalences of O/P and R ratios shown for 3 values of R .

200 when R changes from 1.02 to 1.01. Hence, great care must be taken when making glasses close to the metaphosphate as small variations in formulation and manufacturing conditions can have a big impact on the final result.

A further simplification obtains when considering just the oxygen–phosphorus ratio, O/P . This ratio is helpful in complex glasses with multiple modifiers, particularly those found in different oxidation states. Like R , the O/P ratio reduces to simple values for single Q group types, namely 4, 3.5, and 3 for ortho-, pyro-, and metaphosphate, respectively.

2.2 Mixed Glass Networks

Hybrid glass types are obtained when phosphates are mixed with other oxide glass formers. For the sake of comprehensiveness, it is useful to mention them briefly although these materials are beyond the scope of this chapter. Borophosphates form readily upon melting of boric anhydride and phosphate salts because boron can accept an electron pair and phosphorus can donate one. The $B-O-P$ linkages created between the borate and phosphate units increase the overall connectivity of the network in a way reminiscent of the 3-D open structure of SiO_2 . The great affinity between boron and phosphorus in glasses is reflected by vapor pressures that remain so small above $1000^\circ C$ for a simple borophosphate (BPO_4) [12] that the rate of vaporization remains negligible up to $1450^\circ C$ [2]. The contrast is thus striking with borosilicates or borates for which boron loss can be significant below $1000^\circ C$.

Between SiO_2 and P_2O_5 the structural match is not so good. A phosphate glass typically incorporates up to

about 12 wt % SiO_2 before crystallization occurs, whereas the phosphate solubility in silicates is limited to about 6 wt % P_2O_5 , the insertion of PO_4 tetrahedra into the SiO_4 network normally requiring the association of P^{5+} with charge-balancing cations [13]. As a matter of fact, $Si-O-P$ linkages are not very stable so that they are readily hydrolyzed in water. This intrinsic weakness is turned to an important advantage in bioglasses since phosphosilicates represent a readily available source of PO_4^{3-} ions in solution to contribute to the formation of hydroxyapatite (Chapter 8.4).

Aluminophosphates are also well known. Crystalline $AlPO_4$, which is isostructural with SiO_2 , exemplifies the stability of the $Al-O-P$ linkages also existing in aluminophosphate glasses. Even small additions of Al to a phosphate glass can in fact have a significant effect on properties [14]. Phosphate has also been combined with a wider variety of other formers to make glasses that include sulphur, arsenic, vanadium, or molybdenum.

2.3 Chain Lengths

Initially, simple chemical tests were used to establish that a substance is a polyphosphate, as opposed to a phosphate, such as the ability to coagulate albumen or to react specifically with silver, copper, or zinc. As already noted, however, real advances have resulted from the possibility to isolate specific polyphosphate species first by ultracentrifugation and solubility fractionation and, more efficiently, by 2-D paper chromatography [7]. Resolution of phosphate chains up to 200 units was then made with gel electrophoresis before a wealth of other chromatographic and spectroscopic methods became available.

An important goal of structural studies is the determination of chain lengths. An early method relied on acidity differences between OH groups, depending on the Q^n species to which they belong, namely Q^2 (1 OH, strong acid) or Q^1 (2 OH, one weak and one strong acid). From usual titration curves, it was possible to determine the numbers of strong and weak acid groups and, in particular, to distinguish between cyclic and linear polyphosphates because the former includes only the strong acid groups of Q^2 species. In this way, Graham's salt appeared to be a mixture of linear polyphosphate chains. Other methods to quantifying chain length included solution viscosity, conductivity, and light scattering measurements. Of particular note was the application of the relatively new nuclear magnetic resonance (NMR) spectroscopy by Van Wazer in 1955 [2, 3], which proved to be simpler and more accurate than the end-titration method.

The drawback of these approaches was that they relied on solution techniques. These were fine for sodium polyphosphate glass initially studied, which dissolves very

rapidly in aqueous solutions. For more complex phosphate glasses, however, the rates of dissolution can be extremely low and the temperature or pH changes made to increase them also cause chain hydrolysis, therefore invalidating the measurement. This is why measurements are now directly performed on glasses with a variety of solid-state techniques (Chapter 2.2).

Phosphorus lends itself very well to NMR because ^{31}P provides good signal resolution in a relatively short time. Like for silicates, MAS spectra can provide quantitative information on Q^n speciation (Figure 3) [15] whereas evidence for the interaction of these species is directly drawn from 2-D spectra. Raman spectroscopy can similarly provide information on the ratio of Q species whereas bond lengths and angles as well as coordination numbers are determined with X-ray and neutron diffraction techniques although the complex spectra obtained for glasses with multiple different modifiers quickly become challenging to interpret. In this respect, the availability of a wealth of such data for crystalline phosphates [10] is of great help as a reference framework for the interpretation of glass structures.

3 Synthesis

3.1 Composition Ranges

By usual melt cooling, glasses based on P–O–P networks can be prepared in very wide composition ranges. A number of modifiers and intermediates have been incorporated for P_2O_5 contents ranging generally from ~35 and 65 mol %. They include Li, Na, K, Mg, Ca, Sr,

Ba, Ti, Cr, W, Mo, Cu, Zn, Al, Sn, Fe, Mn, Co, Ag, La, Yb, Nd, Er, or Pb in a list that is by no means exhaustive.

The simplest orthophosphoric acid (H_3PO_4) supercools to form a glass with an unusually low T_g of -121°C [12]. In polyphosphoric acid, where $\text{M}_2\text{O} = \text{H}_2\text{O}$, hydrogen bonds contribute to glass formation. These glasses are model viscoelastic liquids at room temperature where their relatively low viscosities of 10^7 – 10^8 Pa.s make them flow slowly but shatter instead if struck. When water is (largely) replaced by metal oxides, phosphate glasses can exist from pure P_2O_5 to the invert domain provided that the correct modifiers and manufacturing conditions are used. Without very rapid cooling, however, the limit of vitrifiability of about $R = 5/3$ (tripolyphosphate) varies somewhat with the modifier. Whereas 64 mol % can be included for ZnO and 57 mol % CaO [5], the maximum content of K_2O is only 47 mol % beyond which potassium Kurrol's salt $[(\text{KPO}_3)_x]$ crystallizes readily. Upon rapid cooling, these modifier contents can be increased, for example, up to more than 80 mol % ZnO with splat quenching.

3.2 Synthesis

In the laboratory, phosphate glasses are usually synthesized from phosphate salts whose stoichiometry is balanced by P_2O_5 or $\text{NH}_4\text{H}_2\text{PO}_4$ for increasing the phosphate fraction and by metal oxides, carbonates, or hydroxides for raising modifier contents. Some care must be taken in selecting precursors as P_2O_5 reacts exothermically with all basic oxides, sometimes explosively.

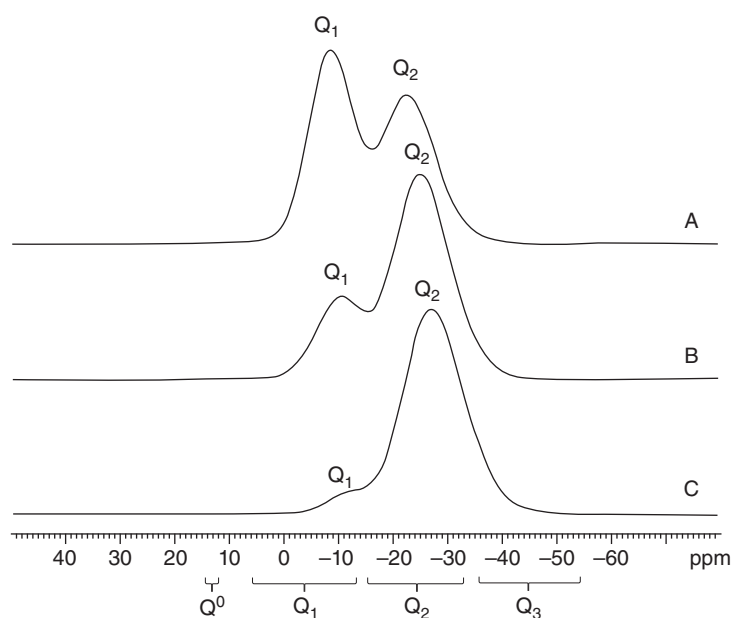
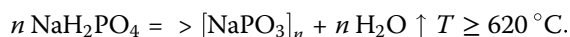


Figure 3 Changes of Q^n speciation as a function of composition apparent in ^{31}P solid-state NMR spectra. Glass compositions (mol %): A = 40 P_2O_5 ·24 MgO·16 CaO·20 Na_2O ; B = 45 P_2O_5 ·24 MgO·16 CaO·15 Na_2O ; C = 50 P_2O_5 ·24 MgO·16 CaO·10 Na_2O . Approximate ppm ranges where the different Q groups occur are indicated by the brackets on the x axis.

The starting mix is heated to temperatures typically higher than 650 °C, sometimes as high as 1400 °C, to trigger condensation reactions whereby polyphosphate chains form and water is expelled as a gas. The reaction of sodium phosphate is for example:



It is of course idealized since NaPO_3 would denote a polyphosphate chain of an infinite length. The length depends on melt composition and is limited by the fact that the developing structure makes it more difficult for water to escape. Its removal can be enhanced by low H_2O partial pressures above the melt, long melting times, or repeated *freezing out*, i.e. alternate crystallization and melting steps, but there is in practice a chain length limit of a few hundred phosphate units. The effects of water are so pronounced that the idea of using different melt times (and thereby having different amounts of entrapped water in the final glass) to differentiate properties was patented. Some speciality glass producers reduce final water levels by utilizing premade polyphosphate salts in their batches, thereby avoiding water that is generated as a result of condensation reactions between simple orthophosphate salts during melting.

The problem of water notwithstanding, phosphate melts are very easy to produce. Fast melting and refining is made possible by their comparatively low viscosities and the fact that they absorb heat rapidly: 90% of incoming radiation at wavelengths higher than 2.5 μm is absorbed within the first $\sim 0.01 \text{ mm}$ of the melt [2]. But precise compositions can be difficult to achieve because of the volatilization of some components. Hence, processing temperatures must be kept low wherever possible to avoid losses that could reach a few % [16] and also depend on phosphate content, type of modifier, and humidity.

An alternative approach to which attention has recently been paid relies on sol–gel wet chemistry (Chapter 8.2). Here, the multistage reaction involves an organophosphate precursor like triethyl phosphate $[(\text{C}_2\text{H}_5)_3\text{PO}_4]$ and an organometallic compound such as calcium methoxide $[\text{Ca}(\text{OCH}_3)_2]$. The advantages are first those of a room-temperature process not needing platinumware and, second, the production of glasses that cannot be obtained from melts (e.g. compositions with extremely low phosphate contents). As for the drawbacks, they are the use of toxic and costly chemicals as well as scale limitations caused by the considerable shrinking of gels upon drying.

3.3 Corrosivity

A particular difficulty in producing phosphate glasses is that their melts are so corrosive that they have been described as *universal solvents* [6]. This feature has stood

them in good stead in applications such as mineral analysis but otherwise causes manufacturing problems. Most ceramics are attacked by phosphate melts, in particular by surface-tension erosion, which implies that the composition of the final glass can be drastically altered by material dissolved from the container. A striking example is that of a sodium phosphate glass, which takes up more than 30 mol % Al_2O_3 when melted in a fused alumina crucible [14]. Quartz is corroded by phosphoric acid itself so that SiO_2 crucibles are also liable to attack from a phosphate melt. Graphite can be an alternative but significant phosphate reduction becomes likely above 350 °C, affecting the structure of the glass and giving it a pinkish hue. Since phosphate melts require an oxidizing environment, graphite is in addition limited by its own oxidation at higher temperatures. Despite such corrosion problems, cost benefits make ceramic melting pots still used for manufacture but great care is taken to record how much container material is incorporated in the melt.

The most resilient materials for handling phosphate melts are noble metals and their alloys. Platinum is good for resisting basic melts, whereas gold fares better for high P_2O_5 formulations. A particular benefit of gold-platinum alloys is their low wetting properties, which reduce the chance of surface-tension-driven corrosion. Platinum alloys can suffer a slight corrosion above 300 °C, however, whose extent decreases with decreasing surface-to-volume ratios. In all cases, an oxidizing atmosphere is needed and contaminants that might cause phosphate reduction must be avoided, since they can result in the formation of platinum phosphides at grain boundaries in the alloy. Because small amounts of contaminants can create significant damage, crucibles must be placed only on clean ceramics. The SiC plates often used in furnaces must be avoided, however, because Si forms a eutectic with platinum so that local alloying could trigger melting of the crucible at a temperature as low as 830 °C.

The potential for electrical circuits involving a melt can also be a source of damage, which is of importance in glass fiber production facilities that use electrically heated bushings. The platinum alloy fiber bushings are cast within an insulation material, which is then placed into a steel housing to support the weight. Ordinarily, the steel box is electrically isolated from the heating system to prevent galvanic corrosion. However, phosphate melts are very good at wetting platinum alloys and can dissolve insulation materials so over time the melt can travel up the bushing tips, across the base plate and insulation and make electrical contact between the busing and the steel housing. The steel is preferentially oxidized as it has a lower anodic index than the platinum. However, this results in phosphate within the melt being reduced, which can then attack the platinum, with subsequent phosphide deposition as previously described.

Corrosion is at its worst at the beginning of the polycondensation reaction when the structure is forming and water is expelled. After this first step, the melt is less aggressive on the container, likely because of a decreased driving force for modifier uptake. Ultraphosphates are bad at ion sequestering, which seems to make them less corrosive but their water sensitivity may require that they be melted in sealed ampoules. The best container for phosphate melts is actually the solid form of the phosphate of interest. Centrally heated furnaces can thus be designed with cooled skins such that the molten phosphate reacts within a chilled skin of the same material as done in a Pochet furnace. With industrial processes, purer phosphate glasses are made in this way than with small-scale laboratory methods.

4 Physical Properties

4.1 The Importance of Field Strength

The effect of modifiers on physical properties depends on their field strength (as described by Dietzel). Higher valences and smaller ions yield stronger P–O–M linkages and, therefore, more significant effects on properties. When only low field-strength modifiers such as Na or K are present, P–O–M bonding is thus weak and glass properties tend to be dominated by polyphosphate chains. With high field-strength modifiers (e.g. Fe, Ti), the reverse holds true because of stronger P–O–M linkages. The crystallization rate is, for example, greatly affected by chain length, whereas the dissolution rate depends heavily on modifiers. A *mixed modifier* effect (–Chapter 4.6) is also known whereby transport properties of glasses with equivalent content of modifiers of the same valence show minimum or maximum values.

4.2 Rheological and Related Properties

Rheological properties are related to the mobility of the glass structure, which depends itself on the chain length of the glass network and the nature of modifiers. With weak P–O–M linkages, the mobility mainly decreases because the phosphate chains become longer, with a resultant modest rise in glass transition and crystallization (T_x) temperatures as well as in viscosity as observed in organic polymers (Chapter 8.8). Above 50 mol % P_2O_5 a network begins to form, which causes a drop in T_g but a significant increase in viscosity. These properties are greatly affected when the structure includes modifiers that create strong P–O–M linkages so that T_g and T_x increase by several hundred degrees. This increase tends to follow a linear trend with modifier content (Figure 4). But certain modifiers exhibit more unusual properties,

Zn- and Sn-bearing compositions having, for example, comparatively low T_g values and viscosities. Typical examples of T_g for a range of binary glasses are provided in Table 1.

Phosphates are Newtonian and generally fragile melts (Chapter 4.1). Their low viscosity makes them prone to crystallization, especially when chains are short. As usual (Chapter 4.1), addition of strong modifiers can increase viscosity by orders of magnitude near the glass transition but this effect diminishes at high temperatures [40] (Figure 5).

A simple indicator of the resistance to crystallization is the difference between T_g and the temperature of the onset of crystallization. The rate of crystallization decreases with increasing configurational entropy because a large number of modifiers make rearrangements of the glass into a crystalline structure more difficult. As a simple example, glass formation can be easier when calcium and magnesium coexist than if only one or the other is present at a lower overall content. In contrast, long chains do not prevent Kurrol's salt from crystallizing from sodium polyphosphate because, with a single modifier type, these chains are equivalent and can thus assemble easily into a repeating crystal structure. Of course, chain length is nonetheless important as indicated by the fact that chains with 6–200 phosphate units usually do not crystallize.

4.3 Volume Properties

With weak modifiers, the glass density decreases as the phosphate content increases and longer chains become more difficult to pack, but it increases as the composition approaches pure P_2O_5 . In contrast, the density generally increases at constant P_2O_5 content when replacing a weak modifier with a strong one (e.g. replacing Na with Ca). The effect is linear, similar to those seen with T_g . At a microscopic level, increasing the electron density in modifiers creates a denser structure through shorter M–O distances but does not cause a change in the average P–O bond distance [8]. The effects of chain length and modifier strength on density are thus opposite, but the latter generally predominates.

Phosphate glasses have comparatively high thermal expansion coefficients (CTE, see Table 1 for some examples) with high values such as the $22 \times 10^{-6} \text{ K}^{-1}$ of the 63.7 P_2O_5 ·9.1 ZnO·24.8 K_2O ·2.4 Al_2O_3 glass of the US patent 3 407 091 [43]. Upon manufacture, such high values can result in significant negative hoop stress, and subsequent deformation, if melts are allowed to cool in crucibles. Annealing is of course required to eliminate residual stress, but phosphates differ from silicates in this respect in two ways. They need to be heated to $\sim 10^\circ \text{C}$ above their dilatometric softening points for effective annealing [5]

Figure 4 The dramatic effect of strong modifiers on glass transition temperature (T_g), as measured by differential scanning calorimetry. Substitution of 12.5 mol % Al_2O_3 or 15 mol % Fe_2O_3 having almost as much effect on T_g as 40 mol % CaO . Average T_g values for binary glasses from Table 1 and trend data from Ahmed [37], Brow [38] and Parsons [39].

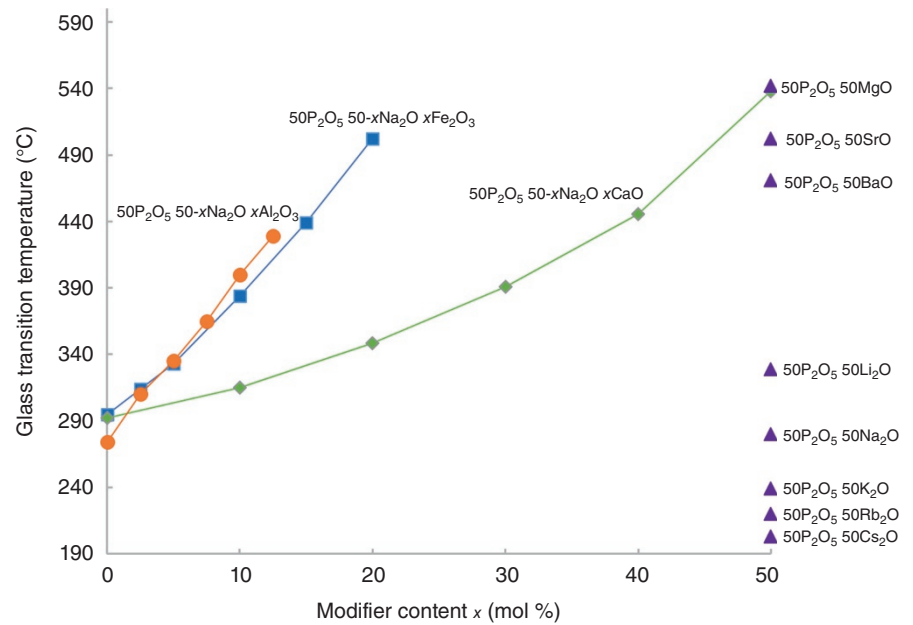


Table 1 Example thermal and optical properties of binary phosphate glasses.

Nominal composition	T_g (°C)	Density (g/cm ³)	CTE (10 ⁻⁶ K ⁻¹)	RI
50 Li ₂ O 50 P ₂ O ₅	322–335	2.35		1.51
50 Na ₂ O 50 P ₂ O ₅	265–295	2.49–2.55	22–24	1.49
50 K ₂ O 50 P ₂ O ₅	213–265	2.41		
50 Rb ₂ O 50 P ₂ O ₅	195–245			
50 Cs ₂ O 50 P ₂ O ₅	170–235	3.50		
50 Ag ₂ O 50 P ₂ O ₅	150–250			
50 BeO 50 P ₂ O ₅		2.32		
50 MgO 50 P ₂ O ₅	520–564	2.43–2.49	7.4–8	1.49–1.50
50 CaO 50 P ₂ O ₅	500–547	2.61–2.69	10–11	1.54–1.55
50 SrO 50 P ₂ O ₅	485–518	3.03–3.30	12–13	1.56
50 BaO 50 P ₂ O ₅	460–482	3.41–3.71	13.4–14.2	1.58–1.59
50 ZnO 50 P ₂ O ₅	400–458	2.82–3.56	6.8–8.0	1.52–2.22
50 CdO 50 P ₂ O ₅	420–450	3.64–3.73	9–10	1.60–1.61
50 PbO 50 P ₂ O ₅	283	4.7–4.79	10.5–13.9	1.72
50 SnO 50 P ₂ O ₅	257–258	3.35–3.49		1.70
50 Fe ₂ O ₃ 50 P ₂ O ₅	492	3.235		
50 CoO 50 P ₂ O ₅		3.02	6.8–7.2	
50 NiO 50 P ₂ O ₅	650			
50 MnO 50 P ₂ O ₅			9.0	
50 V ₂ O ₅ 50 P ₂ O ₅	460	2.79–2.86	8.8	1.80

Source: Compiled from Cha [17], Click [18], Dutta [19], Ehrt [20], Ezz-Eldin [21], Griebenow [22], Hammad [23], Hémono [24], Hermansen [25], Hudgens [26], Lee [27], Liška [28], Mazurin [29], Money [30], Mošner [31], Novita [32], Patel [33], Takebe [34], Tsuchida [35], and Venkateswara [36].

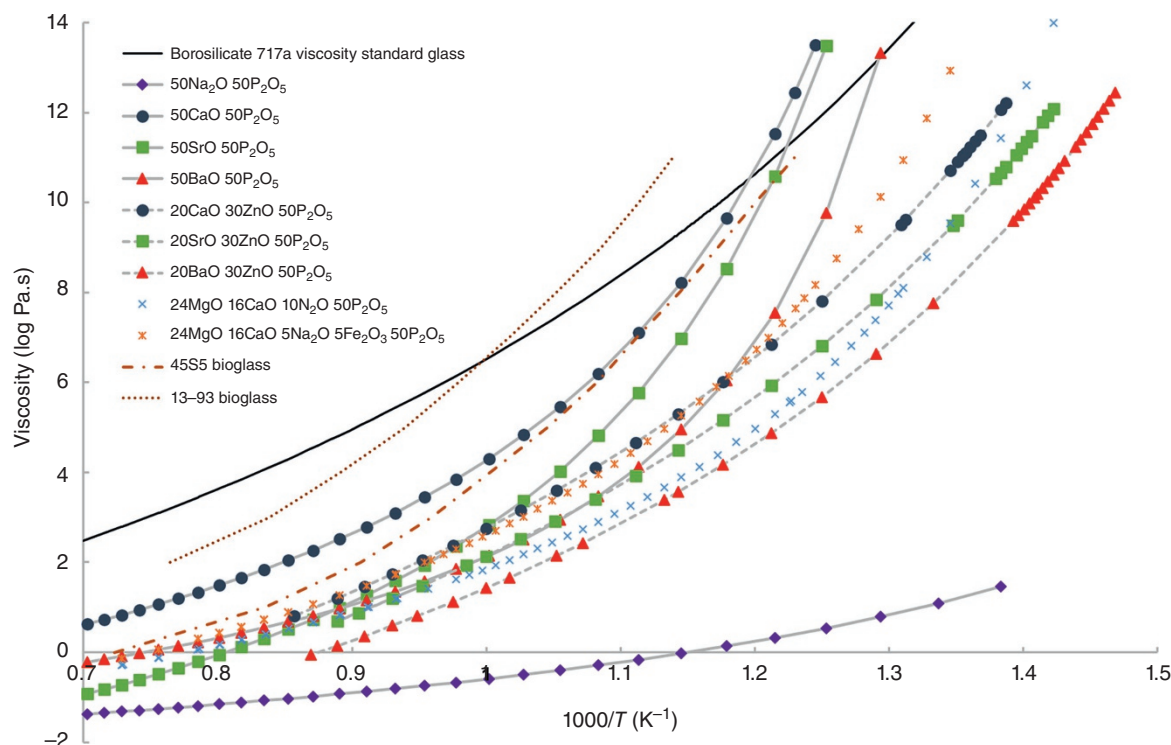


Figure 5 Contrast between the effects of composition on viscosity at high temperatures and near the glass transition. The difference between the weak modifier (Na) and stronger modifiers (Ca, Ba, Sr, Zn, Fe) is stark. Borosilicate standard glass and two well-known bioglasses are provided for comparison. Source: Data assembled from Ehrhart [20], Striepe [41], Döhler [42] and Parsons [40].

and they also require post-annealing cooling rates about twice slower probably because of aging processes of chain structures analogous to those of organic polymers (Chapter 8.7).

5 Optical Properties

5.1 Classical Optics

Phosphate glasses have refractive indices similar to those of silicate glasses but a lower dispersion that places them on the lower left of the Abbe diagram (Figure 6). Because of poor water resistance, their first optical applications made at the end of the nineteenth century by Schott in terms of crown and filter glass did not initially fare well [44]. But a superior UV transmission motivated further research such that Corning filed a patent in 1926 for its UV transmitting Corex glass, containing Al, Ba, and K, before moisture resistance was largely achieved by the 1940s [3]. Glasses produced in 1940 then absorbed both UV and IR light, while transmitting visible radiation, whereas inclusion of iron resulted in windows very effective at absorbing heat. By appropriate formulation of phosphate (and fluorophosphates) glasses, it is now

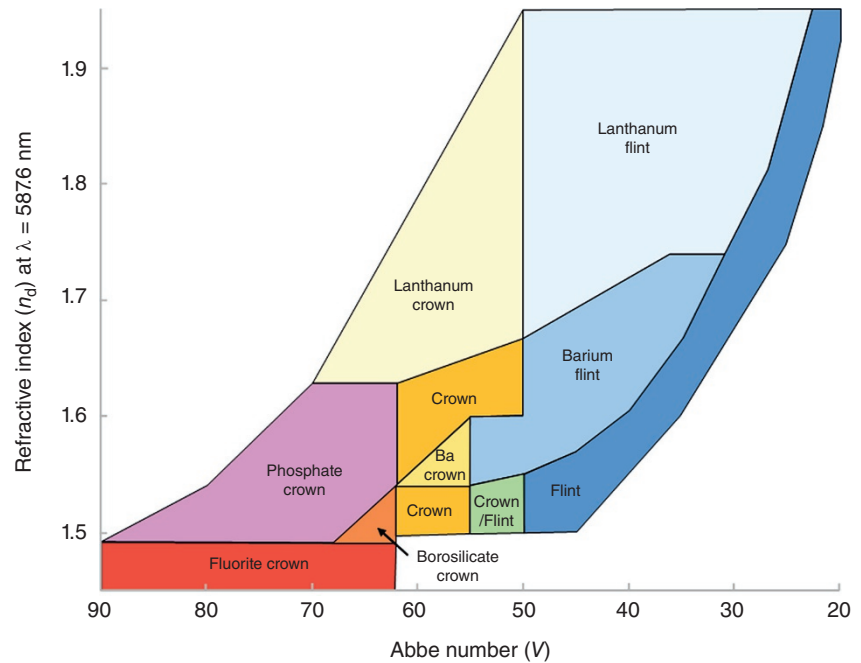
possible to produce spectral filters for a very wide range of wavelengths between about 200 and 1000 nm. Borophosphates also proved interesting in optics as they provide high wetting surfaces, which means that water forms on lenses as a transparent film instead of discrete fogging droplets.

5.2 Rare-earth Doping

Phosphate glasses have filled a particular niche, thanks to the large amounts of rare earths they can incorporate without clustering, which would result in the inactivation of these ions. Whereas silicates can be doped with only a few hundred ppm of rare earths before the occurrence of such a *concentration quenching*, phosphates can contain several percent. As illustrated, glasses bear 18 mol % Er_2O_3 [45]. Such large concentrations of rare earth enables phosphate glasses to be used in fiber amplifiers that are only a few cm long instead of the 20 m of fiber required by silicate glasses (Chapter 6.4). Optical-fiber amplifiers are in development for broadband systems with high-gain, short devices providing on the order of 4.1 dB in only 3 mm [46].

High levels of doping, large emission cross sections, low nonlinear dispersion, low pump thresholds, and

Figure 6 Abbe diagram for a range of different glass types (Chapter 6.1), based on the Schott Glass catalogue. Phosphate crown glasses toward the lower left.



reasonable thermal stability have fostered the extensive use of phosphate glasses in solid-state lasers since the 1970s, initially with Nd [47], then with Er in the 1980s, and more recently with Yb. The glass compositions tend to have more than 50 mol % P_2O_5 to widen the UV range of transparency.

5.3 Laser Systems

Neodymium-doped phosphate is the most common laser glass in use, with the most widely used commercial glasses being LG-750, LHG-8, LG-770, and N31. Nd has four available transitions, with the one of the greatest interest being the ${}^4\text{F}_{3/2} \Rightarrow {}^4\text{I}_{11/2}$ at 1050–1060 nm. Large Nd phosphate laser systems have been used in a number of laser ignition facilities around the world, including GEKKO-XII in Japan, Shen Guang III in China, the Mégajoule Laser Project (LMJ) in France, and the National Ignition Facility (NIF) in the United States. These facilities use extremely high-energy lasers to heat tiny fuel containers in attempts to create nuclear fusion and understand better the mechanisms of nuclear explosions. The laser power of NIF is, for example, 500 TW as reached with 192 beam lines in a parallel system with a total path length of around 1500 m. The 1.85 MJ energy generated within picoseconds yields pressures of 300 billion atmospheres.

Since then the development of silica/phosphate combined laser systems has made reaching powers of the order of 10^{15} W (PW) possible. In 2015, a record high power of 2 PW for 1 ps has been reached in Japan at

FIREX-I, which represented 1000 times the world's total electricity consumption during this very short time frame.

The military is of course interested in laser systems as exemplified by the famous Strategic Defence Initiative (SDI) or *Star wars* program in the United States in the 1980s. With Nd phosphate glass laser, defense technologies have continued to be developed in ground-based systems. A truck-mounted 60 kW laser has been tested recently, although technology has moved toward single-crystal systems that are more robust physically.

In medical and rangefinder applications, Er has been used to produce *eye-safe* laser systems operating at around $1.5 \mu\text{m}$ (${}^4\text{I}_{13/2} \Rightarrow {}^4\text{I}_{15/2}$ transition at 1.53–1.6 μm , depending on host glass composition). Also, spectral glasses have been designed to filter out harmful laser wavelengths. Phosphate laser glasses are produced by companies including Schott (Germany), Hoya (Japan), Kigre (US), and SIOM (China).

Before 1990, the presence of platinum inclusions picked up during the manufacture of phosphate glasses has limited laser size because of damage caused at high peak power, which was eventually making the device unusable and could even affect other components in the optical pathway. Oxidative gas treatments are used to promote their dissolution, generally by bubbling through the melt oxygen or a mixture of oxygen and Cl-containing gases such as CCl_4 or POCl_3 . In this manner, Pt inclusions in phosphate laser glasses are practically eliminated, being fewer than 1 for 10 l of glass. The treatment is also effective at reducing water content, particularly when chlorine is used as it provides favorable



Figure 7 Continuously produced bars of phosphate glass highly doped with neodymium for use in laser cavities at the U.S. National Ignition Facility. Source: Photo public domain U.S. Department of Energy.

equilibrium conditions [48]. As a result, extremely large laser cavities can now be made by continuous processes (Figure 7), whereas surface ion exchange similar to the Gorilla Glass process (e.g. immersion in a KNO_3 melt to exchange small ions on the surface with large potassium ions and thereby creating a compressive surface) has improved two or three times the thermal-shock resistance.

5.4 Phosphate Glass Fibers

In contrast, the use of phosphate glasses as fibers is limited because their *fragile* rheology and high tendency to crystallize make them very difficult to draw. Silicate solutions for optical fibers thus remain preferred, all the more so that phosphates are difficult to integrate into existing infrastructures because of their higher expansivity. Monsanto saw potential in the use of crystalline phosphate fibers in a wide range of nonoptical applications, but this effort was cut short by concerns about environmental impact [6]. Since interest has increased in deliberately degradable fibers for applications such as healthcare, however, facilities for producing phosphate glass fibers have been developed [49]. Phosphate fiber tows and textiles are now produced by the Sinoma company (CN105819697).

5.5 Phosphors

Simplistically, phosphors are solid materials that absorb a particular wavelength of light and then, through radiative

and non-radiative relaxation, emit light at a different wavelength. Such a phenomenon is called photoluminescence. Depending on the material that the phosphor is made from, only specific wavelengths can be absorbed and only specific wavelengths emitted, depending on the band gap structure (Chapter 6.3).

Frequently, this is the conversion of UV to visible light (as is the case with the domestic fluorescent tube). Phosphors have been known since at least the early seventeenth century. An early example was the *Bolognian stone*, a luminescent stone with a BaSO_4 matrix. They have been extremely important in the lighting industry since Becquerel's Geissler tube in 1859 and then Edison's tungsten phosphor electric lamp in 1896. After the end of the Second World War and the advent of equipment for producing UV rays, a dramatic evolution in phosphors occurred, supported by advances in solid-state physics and the understanding of the spectroscopy of solids. The theory of excitation energy transfer and energy levels was clarified through crystal field theory and it became possible to make precise measurements of the multiple close energy levels in trivalent rare earth ions.

The 1940s and 1950s saw the use of manganese, antimony, and tin as phosphors in both silicate and phosphate matrices (the $3(\text{Ca},\text{Sr},\text{Ba})_3(\text{PO}_4)_2 \cdot (\text{Ca},\text{Sr},\text{Ba})\text{X}_2$: $\text{Sb}^{3+}, \text{Mn}^{2+}$ white light phosphor being of particular importance). The era of rare earths (initially Europium) began in the late 60s and early 70s and gave phosphors with very high color-rendering index and luminous flux. The development of better and better phosphors was of course concomitant with the rise of the color television. Phosphates have proved to be good phosphor host candidates, thanks to their low cost, good stability, broad UV transparency, and their range of crystal structures (control of which can shift emission wavelengths, for example, KSrPO_4 doped with Eu^{2+} shows blue emission, while in NaCaPO_4 , it is green). They also are good candidates for the development of strong red emitting phosphors, though current examples of which have low quantum efficiency [50].

The majority of phosphor materials are crystalline powders that are adhered to glass substrates, almost exclusively silicates. Glass has proved to be a very useful substrate, providing both an easily formed shape and the ability to create sealed vacuum vessels, but it has not been greatly used as the host for the emitting species. This is perhaps partially due to the limitations of inclusions possible in silicates, as discussed in Section 5.2. Conversely, phosphate glasses can contain large amounts of dopants without clustering issues, which has contributed to the development of glassy phosphate matrix phosphors.

Early phosphate glass works used similar elements to the crystal phosphors, such as manganese to produce

orange/red light emitting phosphors in zinc phosphate glass hosts [51]. The 70s and 80s brought some analysis of the rare earths but despite the successes of phosphate glasses in laser systems, glassy phosphate phosphors for lighting applications did not see significant research until the mid-2000s. The timing of this is likely related to the breakthrough in solid-state lighting technology that was the bright blue LED, produced by the Nichia Corporation in 1993. By coating this LED with a phosphor that shifted some of the wavelength to yellow, a bright white solid state light was achieved. These offered very high efficiency lighting without the need for mercury vapor. The development of appropriate triphosphors also enabled the use of UV LEDs to produce white light.

Now, phosphates glasses are being considered for white light LED lighting. They make use of the unusually low glass transition temperatures of zinc and tin phosphate glasses to form coatings on LEDs. This replaces the previous materials (usually organic polymers or silicones) and provides better heat resistance, which becomes important in higher powered LEDs. They also offer much simpler production processes, without the need to create crystal powders and adhere them to substrates.

Several glassy phosphate phosphors have been produced with different mixtures of rare earth elements. The combination of the colors produced by these additives (e.g. Dysprosium – blue, Terbium – green, Europium – red) provides white light when excited by UV. Some examples are listed in Table 2. However, with the increasing pressure on rare earth resources and their very localized areas of production, recent papers are looking to revive non-rare earth white light

phosphors by returning to the historical Sb^{3+} , Mn^{2+} systems [52].

As well as the more conventional UV light activated materials, systems have been produced for heat sensing applications whereby IR radiation is converted to visible light [59]. Further, there are ytterbium phosphate glass phosphors capable of converting UV radiation into IR radiation [60], with potential for use in solar cells or in heating.

5.6 Electromagnetic Safety

Some other applications are related to the nuclear industry where lead tungsten phosphate glasses were developed in the 1950s as X- and γ -ray absorbing windows. A particularly neat radiation safety application is the use of silver phosphate dosimeters, produced by the Chiyoda company. Although silver is readily reduced into the metallic state in silicates, it is possible to incorporate 10% Ag_2O into phosphate glasses without problem. If a silver phosphate glass is exposed to γ -rays and then to UV light, the intensity of the visible light emitted is proportional to the γ dose received.

6 Chemical Properties

6.1 Dissolution Mechanisms

As is well known in silicates, dissolution of glass usually occurs through several mechanisms in combination such as hydration, hydrolysis, and ion exchange/

Table 2 Examples of phosphate glass phosphors.

Composition	Excitation (nm)	Emission (nm)	Reference
2.5 SnO, 57.5 ZnO, 40 P ₂ O ₅ , 2 MnO	254	White	Masai [52]
21 SrO, 4 2 ZnO, 37 P ₂ O ₅ , 2 K ₂ O, 0.2 Tm ₂ O ₃ , 0.25 Tb ₄ O ₇ , 1 MnO ₂	360	White	Wang [53]
5 LiO ₂ , 5 Al ₂ O ₃ , 39 ZnO, 50 P ₂ O ₅ , 1 Tb ₂ O ₃	350	545 (green)	Francisco-Rodriguez [54]
5 LiO ₂ , 5 Al ₂ O ₃ , 39 ZnO, 50 P ₂ O ₅ , 1 Tb ₂ O ₃ , 1 Eu ₂ O ₃	318	Red/orange	Francisco-Rodriguez [54]
	359	Warm white	
	340	Neutral white	
98 NaZn(PO ₃) ₃ , 2 Dy ₂ O ₃	349	Neutral white	Caldiño [55]
98 NaZn(PO ₃) ₃ , 2 Eu ₂ O ₃	394	611 (red)	Caldiño [55]
98 NaZn(PO ₃) ₃ , 2 Dy ₂ O ₃ , 2 Eu ₂ O ₃	349	Warm white	Caldiño [55]
	364	Red/orange	
60 NaPO ₃ , 30 Al(PO ₃) ₃ , 5 SiO ₂ , 4 AgNO ₃ , 0.8 Eu ₂ O ₃	360	White	Fan [56]
57 P ₂ O ₅ , 40 ZnO, 3 Tb ₂ O ₃	378	548 (green)	Yaacob [57]
99.5 Zn(PO ₃) ₂ , 0.5 Sm(PO ₃) ₃	344	Orange	Meza-Rocha [58]

selective leaching (Chapters 5.11 and 5.12). The same holds true for phosphates but the mechanisms are quite different. In silicates, the greater stability of Q^4 species has the important consequence that upon dissolution a cross-linked network (with as many Q^4 groups as can be formed) is recreated by reaction of silanol groups to yield colloidal silica particles. In phosphates, the most stable bridging bonds (P–O–P bond) are in contrast found in Q^1 species [61]. Cross-linked structures (i.e. Q^3 species) are very susceptible to hydrolysis and rapidly break down in solution at a rate of about $8 \cdot 10^{-3}$ per minute at 25°C , which is about 1000 times higher than for Q^2 [2]. This feature is referred to as the *anti-branching rule* because it results from the lack of resonance stabilization within the three bonds of the PO_4 tetrahedron (Figure 1). The effect is highly apparent in the very rapid decrease of the viscosity of a solution of ultraphosphate caused by hydrolysis. The Q^3 species are in fact so labile that ultraphosphates absorb water even at $300\text{--}500^\circ\text{C}$.

Because they are much more resistant to hydrolysis, Q^2 species are hydrated and dissolved out as complete polyphosphate chains. Longer chains ($n = 10\text{--}50$) give neutral or slightly acidic solutions, shorter chains ($n = 2, 3, 4$) alkaline solutions (e.g. $\text{Na}_5\text{P}_3\text{O}_{10}$ —pH 9.7). For polyphosphates with only weak, low field-strength modifiers, the main factor controlling degradation is the length of the phosphate chain. As such, polyphosphate glasses with weak modifiers are most durable near the metaphosphate composition as their mechanism of dissolution is almost entirely related to chain hydration. In contrast, strong modifiers can have a very significant effect on glass dissolution.

6.2 Chain Stability

After dissolution, polyphosphate chains are relatively stable in neutral/weak alkali solutions at room temperature. The pyrophosphate dimer, for example, could have a half-life in alkaline solution longer than 2000 years. The stability depends on chain length, decreasing from pyrophosphate down to around $n = 10$ as the electron density of the P–O–P linkages drops from 56 in Q^1 groups down toward 24 for Q^2 species. Above $n = 10$, stability begins to increase again. Chain phosphates are stable under alkali conditions at a pH of about 9, but cyclic metaphosphates are so only in neutral solutions as they open to form linear polyphosphates under alkali conditions.

Although polyphosphates are stable in neutral/alkali conditions at room temperature, they rapidly break down at higher temperatures or under acidic conditions. The degradation rate approximately doubles every 5°C to

increase by a factor of $10^5\text{--}10^6$ from 0 to 100°C and it decreases by a factor of $10^3\text{--}10^4$ from strongly acidic to strongly basic conditions. Mechanical strain can increase hydrolysis rates exponentially. At the roots of these differences is the fact that neutral and alkali conditions cause end-chain scission and cycle formation, i.e. orthophosphate and cyclic trimetaphosphate, whereas random chain scission takes place at pH lower than 4. This is the reason why a highly durable iron phosphate glass with a degradation rate of about $4 \cdot 10^{-8} \text{ kg/m}^2/\text{s}$ at pH 7 can dissolve overnight in a HCl solution.

The durability of phosphate glasses is much enhanced by the incorporation of high field-strength modifiers. These form strong P–O–M linkages either by replacing low field-strength modifiers and linking adjacent phosphate chains, or by breaking down P–O–P linkages, thereby replacing Q^2 with more hydrolysis-resistant Q^1 species. These linkages are partly covalent so that the modifier cations become difficult to displace by selective leaching since oxygen is difficult to protonate with a pK_a lower than 2. As a result, the dissolution mechanism becomes rate-limited by the breaking of these strong P–O–M linkages rather than by chain hydration. Hence, the most durable phosphate glasses are those consisting of very short chains bearing hydrolysis-resistant Q^1 dimers and connected with high field-strength modifiers. A combination of different modifiers can then provide an extremely large range of degradation rates (Table 3).

There are of course similarities between phosphate glasses and polyphosphates in solution. Except for lithium, alkali metal phosphates are highly soluble in water (e.g. $\text{NaH}_2\text{PO}_4 \sim 60 \text{ g}/100 \text{ g}$ at 25°C), whereas almost all other metal cations react to form insoluble precipitates. With polyphosphates, the ability to form complexes means that most metals can be held in solution up to a relatively high limit. This sequestering ability allows phosphate glasses to contain large amounts of modifiers without clustering or crystallization, which is very important in commercial applications of polyphosphates.

6.3 Controlled Ion Release

Many applications of phosphate glasses rely on the ability to take up a large quantity of modifier ions or, alternatively, to release continuously into solution either modifiers or polyphosphate anions. Since degradation can be varied to a large range and is (almost) congruent, control of the rate of ion release is possible.

Probably the best known anion application is Calgon®, a water softener developed in the late 1930s by Hall Laboratories. This was a phosphate glass with a $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$ ratio slightly higher than 1.1 : 1 and a polymerization degree n ranging from 15 to 20. Because it contained only sodium, the glass dissolved very quickly to

Table 3 Degradation rates of phosphate glasses containing different modifiers, measured in deionized water at 37 °C with a surface area to volume ratio $\sim 1.2^\circ\text{--}1.6^\circ \times 10^{-2} \text{ m}^2 \text{ l}^{-1}$.

Glass composition (mol %)	Degradation rate ($\text{kg}^\circ \text{m}^{-2} \text{s}^{-1}$)
50 P ₂ O ₅ 50 Na ₂ O	$3.4^\circ \times 10^{-4}$
50 P ₂ O ₅ 40 Na ₂ O 10 CaO	$8.4^\circ \times 10^{-5}$
50 P ₂ O ₅ 30 Na ₂ O 20 CaO	$2.7^\circ \times 10^{-6}$
50 P ₂ O ₅ 20 Na ₂ O 30 CaO	$3.3^\circ \times 10^{-7}$
50 P ₂ O ₅ 10 Na ₂ O 40 CaO	$1.1^\circ \times 10^{-7}$
50 P ₂ O ₅ 50 CaO	$4.4^\circ \times 10^{-8}$
50 P ₂ O ₅ 40 Na ₂ O 10 Fe ₂ O ₃	$4.3^\circ \times 10^{-8}$
50 P ₂ O ₅ 24 MgO 16 CaO 10 Na ₂ O	$2.2^\circ \times 10^{-8}$
Window glass	$<10^\circ \times 10^{-9}$

Source: Compiled from Ahmed [37] and Parsons [71], Sharmin [72], and Ropp [5].

release anionic chains of polyphosphate in solution. It exchanged with calcium in the water since polyphosphate chains complex much better alkaline earths than alkalis. This ability to sequester ions was monumentally important to the detergent industry and a driving factor in enabling home washing machines and dishwashers. A knock-on effect was an improvement in sewage systems because small quantities of polyphosphate in the water removed the need for grease traps whereas even ppm contents could prevent calcium carbonate (lime-scale) from building up in pipework and boiler systems. Although polyphosphates remain largely unrivalled by organic equivalents, the environmental impact of phosphates and their implication in eutrophication and algal blooms has caused them to be banned in detergents in 1992 in the United States, 2014 in Australia, and 2017 in the EU. Calgon is thus now made of polycarboxylates.

Though detergents have been banned, phosphates are of course widely used in fertilizers. The process of fused calcium magnesium phosphate (FCMP) was developed in 1943 [62], creating a vitreous product by fusion of phosphate rock with magnesium silicate (Mg₂SiO₄, olivine). Although the use of ammonium phosphates and superphosphates dominates the sector, a significant amount of FCMP is used. A glass allows for a slow but continuous release of nutrients, instead of immediately soluble phosphate salts, as a way to reduce phosphate run off and water contamination. In a recent patent, phosphate glass textiles are to be used as root ball nets to provide a static source of fertilizer for young plants.

Perhaps cation-releasing applications of phosphate glasses have been most successful in animal

feeding. The company Bimeda commercializes as COSECURE® pellets of glass fed to cattle. This new kind of *bolus* remains in the stomachs of the ruminants to provide a continuous source of essential trace elements (cobalt, selenium, copper). More recently, other slow-release glasses have been produced for antimicrobial purposes. The product Arglaes® has, for example, been formulated by the company Vitri-Tech to release continuously silver ions, which are effective at killing bacteria.

6.4 Applications to Biology and Food Industry

Phosphates and polyphosphates have a very strong presence in the medical and food industries. This is perhaps not surprising given their importance in biology, in the fabric of DNA and the energy cycle of adenosine triphosphate (ATP). Polyphosphates display antiseptic, cytoprotective, and antiviral activities and have a profound effect on blood clotting. Polyphosphates also interact strongly with proteins, cf. the albumen used as a chemical identifier test for polyphosphate. This interaction is also key to the *coascervation* (separation) of gelatin when tanning leather.

In food, polyphosphates (listed as ingredient E452) perform a variety of tasks. They are among the best-known buffering agents thus used as acidity regulators, thanks to their three acid groups whose *pK* values are widely spaced at 2.1, 7.1, and 12.3. They are good emulsifiers, for example, enabling American cheese to melt without separating. They sequester Ca and Mg, which are required by bacteria, and so prolong the lifetime of food and avoid instances of *Escherichia coli* infection. They can absorb many times their equivalent of water and so provide water retention. They have also been used for their abrasive qualities, for example, in chewing gum and toothpaste.

A neat example of the effects of polyphosphate is instant pudding thickening. It relies on the hydration of sodium pyrophosphate (Na₄P₂O₇), also referred to as tetrasodium polyphosphate, with up to 10 molecules of water. Not only is the pyrophosphate extremely stable at room temperature, but when milk is added, it exchanges Na for Ca to form a stiff crossed-linked gel. Phosphate glasses are also used as leavening agents in baking. From the 1850s, monocalcium phosphate monohydrate (CaH₂PO₄·H₂O) has been used to react with sodium bicarbonate (NaHCO₃) to produce carbon dioxide and obtain the light texture of a foam. But it was not possible to store pre-prepared dough because the reaction is immediate. The solution has been to create a thin glass coating on the surface of the calcium phosphate, which degrades only as the dough is baked at elevated temperatures.

7 Other Applications

7.1 Ion Incorporation

One of the early applications of ion incorporation by phosphate glasses was the *bead test* of mineral analysis. The *microcosmic* salt was heated to form sodium metaphosphate glass, which was used as a “universal solvent” to dissolve mineral samples. The melt was formed on a platinum loop; any trace elements present gave different colors, depending on whether they were in an oxidized or a reduced state. A more recent application of ion incorporation is in the containment of high-level nuclear waste in glass, for which borosilicate matrices are currently predominant (Chapter 9.12). The benefits of phosphates in this application are low melting temperatures to minimize volatilization of radioactive species, low viscosity to improve mixing and homogeneity, and high ability to sequester different radioactive species without phase separation. Low leaching rates, melting temperatures, and crystallization tendencies can be obtained through addition of elements like aluminum and iron, which is why some aluminophosphates are used in Russia [63].

7.2 Seals

The coefficient of thermal expansion of phosphate glasses can be much higher than the high values of $10 \times 10^{-6} \text{ K}^{-1}$ found for lead borate or borosilicate glasses, but are comparable with those of copper, brass, and even aluminum. High-temperature sealing applications have thus been devised to take advantage of these high CTEs in seals operating up to $\sim 500^\circ\text{C}$ or even higher through addition of fillers or partial crystallization. Patents on phosphate sealing glasses (also referred to as solder glasses) have been filed since the 1960s. Compositions make use of the unusual modifier properties of zinc and tin to provide low-viscosity melts that can flow and wet well when melted. These products available from Schott or Corning provide a less toxic alternative to lead-containing borate-based glasses. But a high expansion coefficient is usually at the expense of degradation resistance as strong modifier bonds constrain structural expansion.

7.3 Lubrication

Phosphate ester anti-wear additives have been used in oils for more than 80 years, with the introduction of zinc dialkylthiophosphates (ZDDPs) in the early 1940s [64]. The ZDDP reacts with metal surfaces to create a 50–150 nm wear-resistant iron/zinc phosphate glass layer. Interestingly, the bulk and elastic modulus properties of this layer increase with pressure, which helps the film to maintain its integrity under extreme loads.

However, increasing environmental concerns over phosphates and stricter limits on their use threatens the continued use of these additives.

7.4 Capacitors

Phosphate glasses have interesting electrical properties as well. Barium sodium niobium tungsten phosphate (BaNaNbWP) glasses have demonstrated potential as capacitors through high permittivity values $\epsilon \sim 160\text{--}580$ (cf. silica ~ 4) [65] and high electrical breakdown resistance. Additionally, some silver phosphates have shown promise as solid-state electrolytes, with reported ion conductivities as high as $2 \times 10^{-2} \text{ S/cm}$ at 25°C [66]. By control of oxidation states, semiconductors can be produced using Fe and V glasses.

7.5 Miscellaneous

Polyphosphoric acid glasses have little practical purpose, save for the use of superphosphoric acid with a melting point of 16°C because it allows for easy transport of phosphoric acid for use in high-strength fertilizers.

Phosphate glasses have been used as hydrofluoric acid-resistant labware since 1884 (US 295,410), as phosphate does not form a volatile fluoride like silicates. However, the development of plastic labware has made these applications less valuable.

In metrology, phosphate glass standards might be useful. For viscosity, the borosilicates produced in the mid-90s have now limited stocks and are poor calibrants for phosphate glasses owing to the decades difference in viscosity. Borosilicates may in addition suffer from instability upon extended melting through boron volatilization [40]. The low vapor pressure of borophosphates and a HF-free cleaning process would thus make these glasses good standard materials although their potentially corrosive action on expensive platinumware should be taken into account.

8 Perspectives

Phosphate glasses have benefited from an increasing research over the last two decades to take advantage of their unique characteristics. In addition to the use of modifiers to improve their durability by the introduction of strong P–O–M linkages, recent studies have considered surface modification techniques such as ion exchange (Chapters 3.12 and 6.7). Additionally, treatments with nitrogen compounds to nitride the glass surface have been effective in reducing degradation rates as well [67].

Growing concerns about phosphates in food and the environment may inhibit developments in those areas, or may rather be a boon in establishing glassy polyphosphates as a means of controlling rates of release and reducing excess phosphate. Improved understanding of phosphate biology and development of enhanced biological phosphorus removal (EBPR) techniques could provide a means of effective control of eutrophication [7].

While laser applications are making more use of crystalline materials, phosphors are crucial components in solid-state and thin-film lighting (Chapters 6.9 and 6.10) at a time where enhanced concern for energy saving make efficient lighting more in demand. Current LEDs are encapsulated by organic polymers or silicones, which are limited by heat, UV exposure, and gas permeability. Phosphate glass versions can withstand higher temperatures, are not degraded by UV, and are almost completely gas impermeable. There may also be potential in information storage. Ion and proton transport is also likely to play a significant role in the coming years, contributing to solid-state electronics, batteries, and fuel cells. Other opportunities lie in the use of phosphate glass as lead-free alternatives, for instance, in zero photoelastic constant applications in electric field sensors. There is also significant activity around mass-produced aspherical optics and applications such as IR filter systems in digital photography.

Phosphate glasses in medicine are receiving increasing interest [68] with fibers, composites, and microspheres that are beginning to find applications [69]. High calcium and phosphate contents lend themselves to use in hard tissues and polyphosphates have hemostatic properties. Their optical properties also have potential in phototherapies. Finally, new manufacturing techniques, such as microwave heating [70] and more recent activities looking at blending of glasses, may make for less aggressive melts and realize more use of phosphate glass waste containment.

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7.10

Bulk Metallic Glasses

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1 Introduction

In principle, any liquid can vitrify upon cooling provided that the cooling rate is high enough (Chapter 3.1). However, *high enough* can mean rates as high as 10^8 – 10^{10} K/s required for pure metals like V, Fe, or Co, with the consequence that the amorphous materials that can be obtained and stabilized versus crystallization even at room temperature are only nanometric spheres [1]. For obvious structural reasons (Chapter 3.1), pure metals are actually among the worst glass formers.

Hence, it was a real breakthrough when Pol Duwez (1907–1984) and his collaborators in 1960 vitrified an Au–Si liquid at a rate of about 10^6 K/s in the form of splat-cooled flakes [2]. This first Au–Si glass was a chance discovery because the actual goal of the experiments was to quench in the form of crystalline solid solutions binary metal liquids that separated into two different crystals even upon relatively rapid cooling. Understanding at once the importance of the new glass family, Duwez and his team members then showed that vitrification could be achieved in other metallic systems, such as Fe–P–C [3], especially when a metalloid was added to Fe in a 25 : 75 or 20 : 80 ratio. From a physical standpoint, in these metallic glasses they observed ferromagnetism, relatively high electrical resistivity, superconductivity, and other properties existing in crystals while noting otherwise some unusually high resistance to chemical attacks by acid and other corrosive solutions.

These unexpected findings raised fundamental issues, at the same time they paved the way to valuable applications. High mechanical properties resulted from the lack of dislocations and grain boundaries existing in crystalline metals, whereas the extremely low hysteresis losses of ferromagnetic glasses would later be used to reduce energy losses in the electrical transformers. Significant efforts had to be done, however, to improve the glass-forming ability (GFA). The solution was to optimize the chemical composition of the starting melts so as to produce real bulk glasses as three-dimensional objects with the size of at least 1 mm in every spatial dimension needed for practical applications.

Many different alloys have been investigated so far for this purpose, based on rare-earths, Mg, Zr, Ti, Fe, Co, Pd, Pt, Au, Ag, Cu, Ni, or Ca. The outcome of this extensive work has been the production of many different metallic glasses of 1–100 mm characteristic size [4, 5] with methods that include fluxing for a Pd–Ni–P glass of centimeter scale was then produced in the 1980s by fluxing [6]. Besides, hard and soft ferromagnetic alloys based on Nd and Fe or Co, respectively, were also produced and studied [7]. Since then these *bulk* glasses (Table 1) have found their ways in a wide range of products such as sports goods, watches, electromagnetic-wave shields, optical devices, power inductors, mini transformers, micro-gear motor parts, pressure sensors, Coriolis flow meters, coating materials, or medical instruments. From a practical standpoint, an additional advantage has been the possibility to cast metallic glasses with available processes, which include the economically efficient *net-shape casting* technique, thanks to which accurate dimensions and high surface quality are achieved without subsequent machining.

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Table 1 Representative metallic glasses: alloy systems and important mechanical and other properties, including typical (D_t) and maximum (D_m) critical ingot diameters.

Alloy system	D_t, D_m (mm)	T_g (K)	Yield strength (GPa)	E (GPa)	HV
Zr–Cu–TM–Al	~10, 20	650–750	~1.7	80–90	480–550
Pd–Cu–Ni–P	~20, 80	550–600	~1.5	80–95	480–520
Ti–Cu–Sn–TM	~3, 7	600–700	~2	95–105	~650
Mg–Cu–RE	~10, 25	400–450	0.7–0.9	45–55	280–310
Ca–Mg–Al–TM	~5, 10	400–500	~0.35	20–35	~150
La–Cu–Al	~5, 20	400–450	0.6–0.9	30–45	200–250
Fe–Co–TM–ME	~5, 15	800–950	~4	~200	900–1000

RE, rare-earth metal(s); ME, metalloid(s); TM, other transition metal(s).

To review these various features, the present chapter will first discuss the glass formation mechanism. Next, the structure of metallic glasses will be discussed. Mechanical properties and the formation of shear bands upon stress will then be presented before the deformation mechanisms are discussed in more detail, particular attention being paid to the plasticizing function of nano/microscale crystalline phases that can precipitate within the overall amorphous matrix. Soft and hard magnetic properties and applications will be finally reviewed along with structural, chemical, and other specific uses of metallic glasses. This chapter is by no means comprehensive owing to the impressive size now reached by the literature on metallic glasses. Interested readers are thus referred to available monographs for more detailed accounts [8, 9].

2 Glass Formation

2.1 Vitrification Criteria

Metallic glasses deserve their names because they display upon cooling or subsequent heating the conspicuous features of a glass transition, namely, abrupt increases in the specific heat capacity (C_p) and thermal expansion coefficient (α) in relatively narrow temperature intervals. On heating the glass above the glass-transition temperature T_g , the supercooled liquid forms and generally begins to crystallize at a temperature T_x well before the stable liquid domain is reached at the liquidus temperature T_l (Figure 1). Upon heating at rates on the order of 10^1 K/min, the T_g values observed in these measurements are close to the temperatures at which the viscosities of the supercooled liquid are about 10^{11} – 10^{12} Pa·s.

In spite of their chemical diversity, bulk metallic glasses share three other features [4]: (i) they, in general, belong to multicomponent systems that ensure large enough

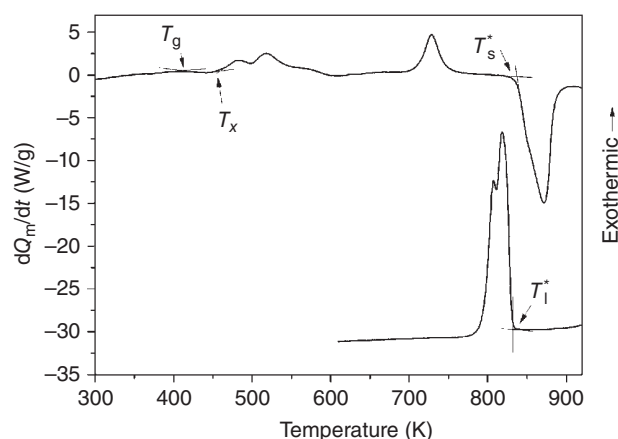


Figure 1 A typical DSC thermogram of a metallic glass crystallizing through metastable stages: glass-transition temperature (T_g), onset temperature of crystallization (T_x), several exothermic peaks, endothermic melting peak on heating and exothermic peak on cooling and approximate liquidus (T_l^*), and solidus (T_s^*) temperatures. The heating and cooling rates were different.

configurational entropies and, therefore, freezing-point depressions as deep as possible (Chapter 5.2) and viscosity increases as fast as possible on cooling; (ii) their constituent elements have significant atomic size ratios exceeding 1.12 so as to ensure high packing density between “solvent” and “solute” atoms; (iii) and enthalpies of mixing in the systems are largely negative.

These criteria need to be satisfied to achieve not only a good GFA but also a relatively high thermal stability against crystallization. Complex chemical compositions not only allow relatively high viscosities but also make crystallization more difficult by increasing the number of potentially precipitating crystal line phase. In an anthropomorphic way, the effect is expressed by the *principle of confusion*: upon continuous cooling, the liquid finds itself frozen into a glass before having had enough time to choose which of these crystals competing for nucleation and growth would actually form. As an

example, the good GFA of the Fe–Cr–Mo–C–B–rare earth liquids has been assigned to the low growth rate of the χ -Fe₃₆Cr₁₂Mo₁₀ phase along with the destabilization of competing crystalline phases that would form by eutectic crystallization [10].

Without being of universal validity, the following three parameters are useful to characterize more precisely glass formation. They can be determined most conveniently from differential scanning calorimetry thermograms (Figure 1). The first two are the reduced glass-transition temperature, $T_{rg} = T_g/T_l$, and width of the supercooled liquid region, $\Delta T_x = T_x - T_g$. Bulk metallic glasses are then obtained in a narrow 0.5–0.65 range of T_{rg} values whereas ΔT_x vary much more with composition from about 15 to 120 K. These two parameters have been combined into the third, $\gamma = T_x/(T_g + T_l)$, which appears to discriminate better the alloys with good GFA by values ranging from about 0.35 to 0.45 [11]. Many similar parameters were further developed later [12]. Also, in metallic as in other kinds of systems, liquids with high fragility (high parameter m) are generally not good glass formers because, for a same reduced T_{rg} , they have lower viscosities between T_g and T_l and, therefore, higher crystal nucleation and growth rates with the exception of relatively fragile Pd–(Ni, Cu)–P glasses that have extremely large T_{rg} values [13].

2.2 Glass Transition

The glass-transition temperature is usually measured by calorimetry on heating. For iron-based glasses, T_g is as high as ~900 K but it is close to room temperature for Ce- and Ca–Li-based glasses and as low as 308 K for Ca₆₅Li_{14.54}Mg_{12.46}Zn₈ [14].

As usual (Chapter 3.6), the specific heat capacity C_p of a metallic glass near the room temperature follows the Dulong and Petit law of 3R per mol and is slightly higher than that of the crystalline counterpart (Figure 2). In general, the C_p increase on heating in the glass-transition region is as abrupt as in other glass-forming systems. For some Zr- and Au-based alloys, some unusual features can nonetheless be observed in step-scan measurements when relaxation sets in [15]. These particular features are two successive sigmoidal-type C_p increases upon heating that cause the C_p difference between the supercooled liquid and the crystal to reach about 60%. With only a slight hysteresis, these variations are largely reversible upon cooling (Figure 2). Such a two-step glass transition at around 340 and 380 K is likely related to differences in the temperature dependences of diffusion coefficients within the glass. At lower temperatures, diffusion by atomic hopping would be several orders of magnitude faster than by cooperative shearing so that it is the only process involved at the onset of atomic mobility at

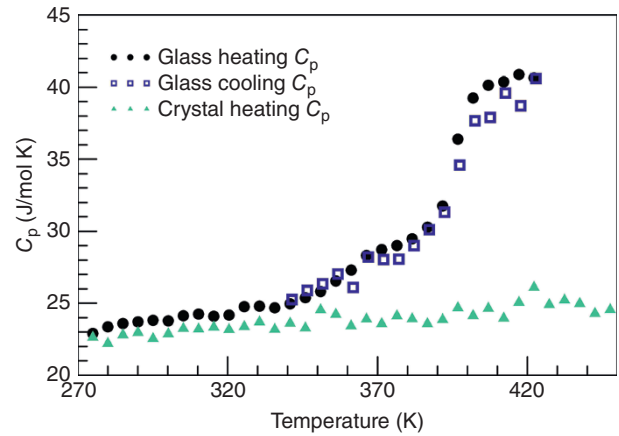


Figure 2 Two-step glass transition of Au₄₉Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3} in heat-capacity measurements made at 5 K/min upon both heating and cooling. Data for the crystalline state are included for comparison. Source: Reproduced from [15] with permission of Elsevier.

the first transition. With increasing temperature, however, the kinetics of cooperative shearing eventually catches up to cause the second transition. Hence, an interesting consequence of the process is that the mobility of different elements of the alloy freezes in at different temperatures starting from larger atoms with lower diffusivity.

On heating up to T_g , the glassy structure relaxes, making the samples more dense and brittle. However, one can achieve an opposite process of structural rejuvenation by heating the glass above T_g and then fast cooling [16]. Structural rejuvenation is also achieved by cryogenic cycling [17].

2.3 Vitriification Versus Crystallization

As usual, the vitrifiability or GFA of alloys is determined by intrinsic and extrinsic factors (Chapter 5.4), being, for example, limited by homogeneous or heterogeneous crystal nucleation [18], respectively, and by modification of the cooling rate. Extrinsic factors are related to inclusions or dissolved impurities in the melt, poor finish, or cleanliness of the mold surface that reduce the cooling rate, turbulent flow during solidification, etc. [19]. The GFA of some metallic glasses is promoted by the use of oxide fluxes. Such an efficient flux is molten B₂O₃ for Pd-based glasses and other systems in which the size of amorphous samples is increased, thanks to suppressed heterogeneous nucleation [6]. The point is also well illustrated by Al-based glasses for which the use of an MgCl₂–CaCl₂ flux allows their critical casting thickness to be increased from about 1 mm to a record value of 2.5 mm for the Al₈₆Ni_{6.75}Co_{2.25}Y_{3.25}La_{1.75} composition [20].

Heterogeneous nucleation is by definition peculiar to the process involved. Hence, homogeneous nucleation deserves more attention in view of its general nature. For metallic glasses, however, the boundary between homogeneous and heterogeneous nucleation can be somewhat blurred because one cannot always avoid upon glass formation the formation of a quasicrystal nuclei or even of crystal – an example of growth-rate-controlled glass is given in [10]. In these cases, crystals can grow readily upon heating as revealed by the exothermic signals present in thermograms.

In a general way, four kinds of processes are distinguished for crystallization. In the simplest, the precipitates are either isochemical with the starting metallic glass (polymorphic reaction) or not (primary crystallization). During eutectic crystallization, two or more phases nucleate and grow conjointly (Chapter 5.2). In the fourth case of spinodal/binodal decomposition (Chapter 5.2), the crystallization process is preceded by liquid–liquid (or glass–glass) phase separation. In all cases crystallization is a spontaneous process, which lowers the Gibbs free energy (G) of the system. According to the classical nucleation theory (Chapter 5.4), the growth of a nucleus of radius r is first opposed by the creation of interface energy (along with elastic-deformation energy), until the radius exceeds a critical value r_c from which the negative volumetric ΔG caused by the crystallizing fraction predominates. The nucleation and growth rates have different temperature dependences. The number of critical-size nuclei per unit volume is proportional to $e^{-\Delta G_c/RT}$, where ΔG_c is the Gibbs free energy of formation of a critical nucleus, which depends on the extent of supercooling. On the other hand, the frequency of atomic transfer through the interface is proportional to $e^{-Q_N/RT}$. Hence, the nucleation rate I is:

$$I = I_0 \cdot e^{-Q_N/RT} \cdot e^{-\Delta G_c/RT}, \quad (1)$$

where $Q_N \sim 1/\Delta G^2$ is the activation energy for transfer of the atoms across the surface of a nucleus. The growth rate (u) is proportional to the frequencies of the transition from liquid/glass ν_{l-s} to solid and back, ν_{s-l} with

$$\nu_{l-s} = \nu_0 \cdot \exp.(-\Delta G/RT). \quad (2)$$

For interface-controlled growth with the activation energy Q_g , the rate thus is:

$$u = u_0 e^{-Q_g/RT} \cdot (1 - e^{-\Delta G/RT}), \quad (3)$$

If I and u are time independent and the reaction is interface-controlled, the kinetics of the nucleation and growth of spherical crystals can be analyzed in terms of the Kolmogorov–Johnson–Mehl–Avrami theory (Chapter 5.4). The general exponential equation for the fraction transformed x then is:

$$x(t) = 1 - \exp((-\pi/3)Iu^3t^n), \quad (4)$$

where n is the Avrami exponent. The time–temperature-transformation diagrams created in the isothermal mode or under continuous heating are useful for comparing the thermal stabilities of different glasses [9].

One finds that reduced supercooling (undercooling) before crystallization from the melt is the smallest for easily nucleating quasicrystals, larger for crystal approximants and the largest for crystalline phases [21].

2.4 Density and Entropy

The density of a liquid increases faster with temperature than that of its crystalline counterpart. By analogy with the well-known Kauzmann's entropy crisis [8], a supercooled liquid would thus become the densest phase at some temperature if the glass transition was not taking place. For liquid Ni and Fe, quantum mechanics [22] as well as classical [23] molecular dynamics simulations have indeed predicted vitrification at temperatures slightly higher than that of such a density crisis. One should remember that FCC structure of Ni and γ -Fe (as well as HCP) is the densest possible packing of singular-type atoms.

2.5 Viscosity

The viscosity of a supercooled liquid changes drastically with temperature, especially close to T_g . Although the transition takes place in a temperature interval, an arbitrary glass-transition point is defined as a temperature at which the viscosity of a liquid reaches 10^{12} Pa·s on cooling. For some materials this value belongs to the glass-transition region defined by C_p measurement, but it is not the case for others [24].

Recent studies have emphasized the importance of the electronic structure. For example, stronger covalent bonding between metal atoms and phosphorus has been observed in Pd–Cu–Ni–P melts cooled down close to the glass transition. In turn, this stronger bonding causes structural changes in the liquid alloy that result in a more fragile character of the temperature dependence of its viscosity [25].

2.6 Thermal and Electrical Conductivity

Thermal conductivity is a fundamental property in glass formation since it controls the rate at which a liquid is cooled and, therefore, the critical casting thickness. A disordered structure generally impedes to some extent thermal conduction (Chapter 4.5). The thermal diffusivity/conductivity of amorphous alloys conform to this rule

Table 2 Room-temperature electrical conductivity, thermal diffusivity, and thermal conductivity of bulk metallic glasses [9].

Alloy	Thermal diffusivity (mm ² /s)	Thermal conductivity (W/m·K)	Electrical conductivity (μΩ·m) ⁻¹
Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀	1.62	5.11	0.541
Zr ₅₅ Al ₁₀ Ni ₅ Cu ₃₀	2.2	5.02	0.53

since they are slightly smaller than those of their crystalline counterparts and they slightly increase with temperature. As also expected, the typical room-temperature values listed in Table 2 are several times higher than for oxide glasses (Chapter 4.5), consistent with the differences between metallic and mixed ionic/covalent bonding between these phases [19].

Likewise, the electrical conductivity of metals is lower in the amorphous than in the crystalline state. Typical values of the electrical resistivity are 1–3 μΩm (Table 2). Some metallic glasses do exhibit moderate decreases of the electrical conductivity with temperature, but less simple variations are observed in alloys such as Pd₄₀Ni_{40-x}Cu_xP₂₀ for which the temperature dependence changes from positive to negative when the Cu content exceeds 15 % [26]. A similar change takes place in the Pd–Ni–P system when the P content becomes more than 24 %.

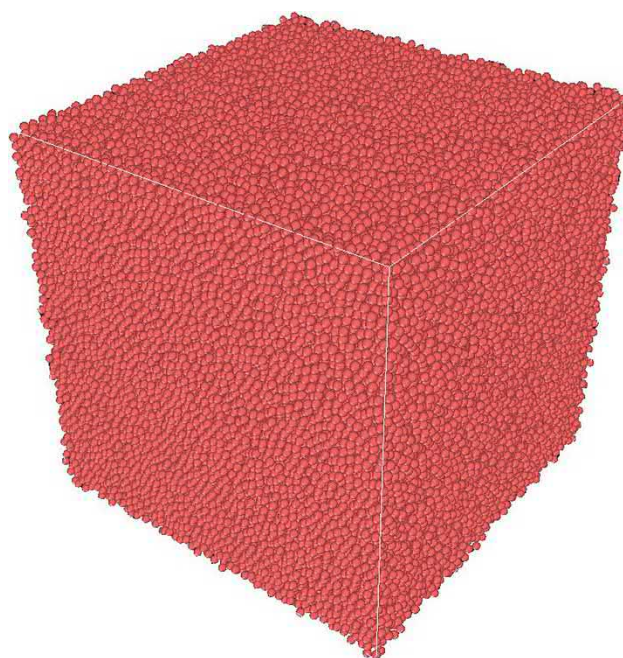
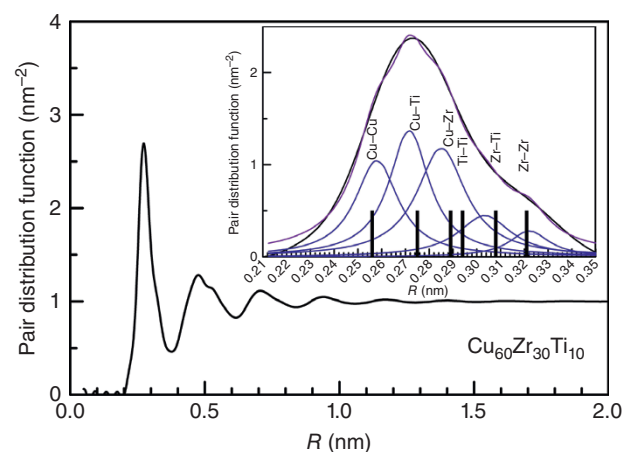
3 Structure

3.1 Short-range Order

As determined by diffractometry (Chapter 2.2) or computer simulations (Chapter 2.8), the structure of metallic glasses differs in many respects from that of network-building oxides (Chapter 2.5). The small density differences between metallic glasses and their crystalline counterparts have made clear that the former phases consist of efficiently packed clusters rather than of dense random packing of atoms. Atomic clusters about 1 nm size have been directly observed by scanning tunneling microscopy [27] whereas medium-range order zones and even nanocrystals are present in some glassy alloys.

Atomic short-range ordering is also seen in molecular-dynamics simulations of Fe (Figure 3). In an amorphous Cu–Ti–Zr alloy (Figure 4), the first peaks are assigned to well-defined interatomic interactions whereas some order persists up to about 1–2 nm [28].

Interesting correlations between such structural changes and non-Arrhenian rheology have been made

**Figure 3** Room-temperature cell of glassy Fe produced by a molecular-dynamics simulation of a set of 128 000 atoms.**Figure 4** Pair-distribution function of a Cu–Zr–Ti alloy determined from synchrotron X-ray diffraction experiments [28] and fitting of its first maximum with 6 Gaussian peaks (inset). Reproduced with permission of Elsevier.

for a Pd–Cu–Ni–P melt where both Ni and Cu form strong covalent bond with P through p-d hybridization whereas Pd–Cu–Ni interactions are metallic. When plotted against temperature, the ratio between the areas of the (Cu, Ni)–P versus Pd–(Ni–Cu) and Pd–Pd peaks of the pair-distribution function (PDF) changes on cooling down to the glass transition below which it remains constant (Figure 5) [25]. In other words, the proportion of (Ni, Cu)–P clusters remains constantly low in the glass range. Then it increases in the liquid phase on heating,

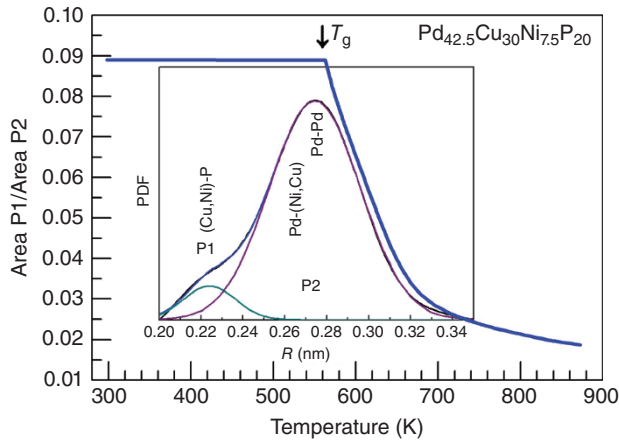


Figure 5 The first two Gaussian peaks at 298 K of the pair-distribution function of a Pd–Cu–Ni–P glass and the rapid decrease of their area ratio above the glass transition temperature. Alloy vitrified under vacuum and studied by X-ray diffraction at a synchrotron facility in-situ on cooling. *Source:* Data from [25] with permission of the American Institute of Physics.

causing the rheology to be non-Arrhenian because this disruption of short-range order results in a decrease of the activation energy for viscous flow.

3.2 Structural Heterogeneities

Most metallic glasses have a uniform structure at a scale larger than about 1–2 nm (Figure 6) as shown by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (Chapter 2.3) [28]. However, atomic clusters and phase separation in some alloys lead to the locally inhomogeneous structure found in Pd-based glass, for example [29]. Surface heterogeneities may also exist [30], like those observed on the $\text{Au}_{49}\text{Cu}_{26.9}\text{Ag}_{5.5}\text{Pd}_{2.3}\text{Si}_{16.3}$ glassy rods that have a thin crystalline surface layer, consisting of grains of an Au-based solid solution embedded in the amorphous phase. Whereas this solution gives a nice yellow color to the sample surface, the internal part of the ingot is metallic gray owing a relatively high Si content [9].

3.3 Phase-separated Glasses

Another important feature is the solid- or liquid-state immiscibility (Chapter 5.2) that prevails in some metallic systems. Solid-state immiscibility between Zr and Nd causes a phase separation in the Zr–Nd–Al–Ni system. A globular phase in the $\text{Zr}_{30}\text{Nd}_{30}\text{Al}_{15}\text{Ni}_{25}$ alloy is Nd-rich whereas the surrounding matrix phase is Zr-rich (Figure 7) [31]. The elongated Zr-rich phase with the nominal $\text{Zr}_{53.0}\text{Nd}_{9.2}\text{Al}_{13.9}\text{Ni}_{23.9}$ atomic composition produces a larger halo ring in a SAED pattern, whereas the second glassy phase is Nd-rich with the $\text{Zr}_{17.8}\text{Nd}_{43.4}\text{Al}_{16.1}\text{Ni}_{22.3}$ composition.

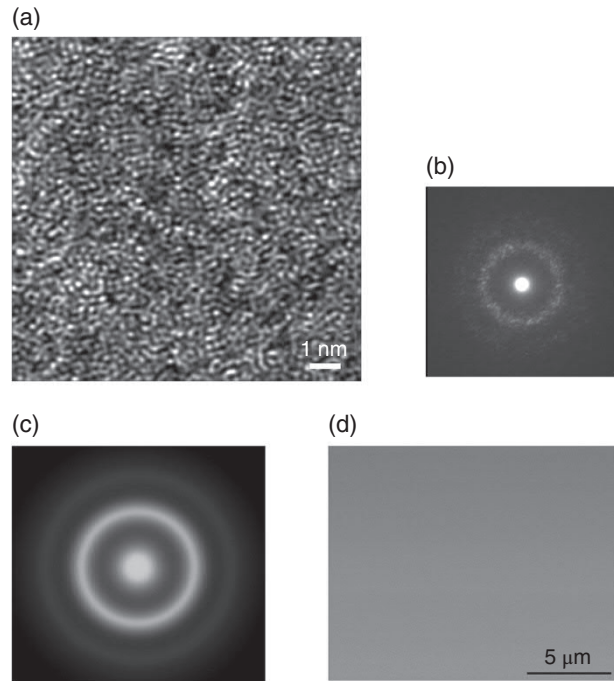


Figure 6 The structure of $\text{Zr}_{62.5}\text{Cu}_{22.5}\text{Fe}_5\text{Al}_{10}$ glass directly observed by electron microscopy. (a) Typical HRTEM image indicating an atomically disordered structure. (b) Nanobeam and (c) selected-area electron diffraction patterns. (d) Homogeneous structure apparent in a backscattered-electron SEM image.

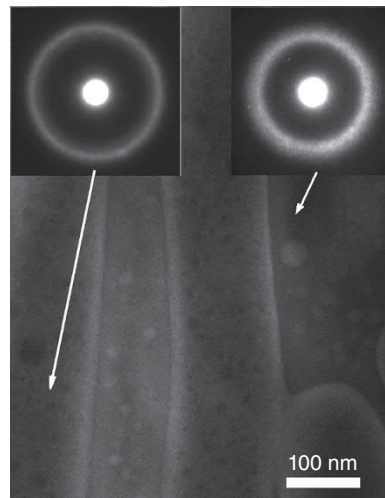


Figure 7 Bright-field transmission electron micrograph showing a two-phase structure of the $\text{Zr}_{30}\text{Nd}_{30}\text{Al}_{15}\text{Ni}_{25}$ glass and the relevant selected-area electron diffraction patterns. *Source:* Reproduced from [31] with permission of Elsevier.

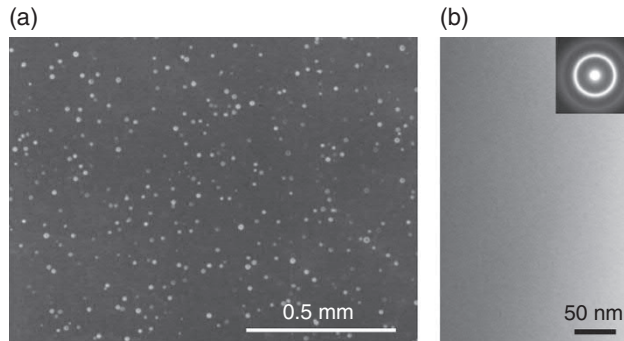


Figure 8 Electron-microscopy micrographs of a porous $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$ glass. (a) SEM image of the porous structure obtained from an initial H_2 pressure of 15 MPa. (b) Bright-field TEM image of the glass matrix whose selected-area electron diffraction pattern is also shown.

3.4 Porous Glasses

Open- [32] and closed-pore [33] type glassy alloys are produced in metallic systems. Owing to their low density, these metallic glasses with open or closed porosities are very promising materials for structural applications. Their porosity is created by the precipitation of a hydrogen gas initially dissolved at some high pressure into the liquid $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$ alloy [33]. The pore size and distribution are then controlled by the pressure drop during foaming and cooling. The hydrogen dissolved is released as bubbles, which are small and evenly dispersed if foaming takes place at about 10% of the dissolution pressure (Figure 8). For larger pressure drops, larger pores and, thus, higher porosities are obtained. A similar result with a porosity of up to 10% is achieved if the porous glass is reheated in the supercooled liquid region to let the bubbles expand. Anticipating the following section, we note at once that the mechanical properties of porous samples can be improved as indicated by the strain–stress curves of the aforementioned Pd–Cu–Ni–P glass (Figure 9). With an existing porosity, the yield strength is only slightly reduced whereas the compressive plasticity of the porous sample is much higher (Figure 9). A 5.7% porous sample has, for instance, a $\sigma_{0.2}$ value of 1420 MPa, a Young's modulus of 88 GPa, and a plasticity of about 19%. The ductility of the glass is greatly improved by a control of the pore size and volume fraction.

3.5 Nanostructured Materials Produced by Thermal Crystallization of Metallic Glassy Phase

At large supercooling, a nanostructure can develop in an overall amorphous matrix if the rate of crystal nucleation is rather high while the rate of crystal growth is low. The phenomenon is common upon primary crystallization of

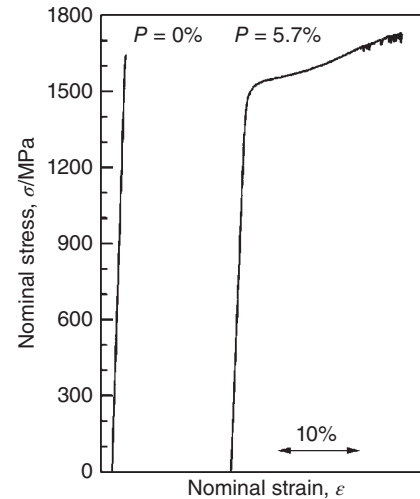


Figure 9 Comparison between the compressive stress–strain curves of porous (5.7% porosity) and pore-free Pd–Cu–Ni–P glassy sample ($P = 0\%$).

glasses with a long-range diffusion-controlled growth. Nanocrystals can then represent barriers for the deformation of the glassy matrix but their efficiency to block the shear deformation, of course, depends on their size and volume fraction [8].

Quasicrystals are quasiperiodic in one, two, or three dimensions but their diffraction symmetries are forbidden in real crystals because they lack 3-D translational periodicity. In various metallic glasses, one observes on heating the formation of *icosahedral* quasicrystals described by a six-dimensional space group, which characterizes the symmetries of the icosahedron (the regular 20-face polyhedron). These icosahedral quasicrystals, for instance, form upon annealing of $\text{Hf}_{65}\text{Pd}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ glass where they show diffuse boundaries with the glass matrix (Figure 10) [30].

These quasicrystals are also found in Zr–Al–Ni–Cu–Ag, Zr–Al–Ni–Cu–Pd, and various other systems as a Cu-based icosahedral phase is observed after heat treatment in Cu–Zr–Ti–NM alloys (NM denotes noble metals) containing Pd and Au [9].

4 Mechanical Properties

4.1 High vs. Low Temperature

On heating up to slightly above T_g , metallic glasses first exhibit a non-Newtonian flow before becoming Newtonian in the supercooled liquid region. As usual, the boundaries between three ranges of inhomogeneous deformation, non-Newtonian flow, and finally Newtonian flow shift toward lower temperatures when the

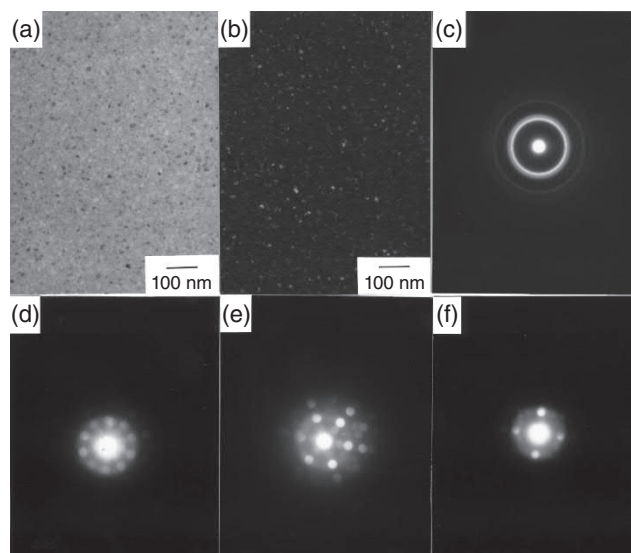


Figure 10 Electron microscopy micrographs of icosahedral quasicrystals in the $\text{Hf}_{65}\text{Pd}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ glass annealed for 600 s at 873 K. (a) and (b): bright- and dark-field TEM images; (c) selected-area electron diffraction pattern; (d)–(f): five, three, and twofold symmetries, respectively, apparent in the nanobeam diffraction patterns. Source: Reproduced from [30] with permission of the American Institute of Physics.

loading rate decreases because the timescale of the experiment then becomes shorter compared to the intrinsic structural relaxation times of the material. Little needs to be said about Newtonian flow, which involves only quick structural rearrangements in the liquid. Attention will thus rather be paid to the mechanical responses of metallic glasses below the glass transition temperature and to the modes of deformation of the materials, which can be complex.

4.2 Quasi-static Room-temperature Properties

Not surprisingly, metallic glasses have the excellent mechanical strength. Owing to their dense atomic packing, their elastic constants do not differ much from those of their crystalline counterparts. A high hardness is combined with good wear resistance and large elastic deformation with strengths of about 2 GPa for Cu-, Ti-, and Zr-based glasses as well as of about 3, 4, and 5 GPa for Ni-, Fe-, and Co-based glasses, respectively. For example, Co–Fe–Ta–B glass has a ultrahigh fracture strength exceeding 5 GPa whereas the tensile strength of Co–Ta–B glasses approaches 6 GPa. Most of these glasses are brittle since, with a small number of exceptions [34], they are not ductile in tension. Hence, many of them fail when the elastic deformation limit is exceeded although some can be deformed plastically upon room-temperature compression.

A noteworthy phenomenon is that some extremely strong glasses in the as-cast state become brittle when annealed close to the glass transition or even after a long period of time at room temperature. For $\text{Zr}_{50.7}\text{Cu}_{28}\text{Ni}_9\text{Al}_{12.3}$ glass, however, this *embrittlement annealing* has been opposed by the deposition of a crystalline W coating, which preserves the excess volume of the material and enhances both its strength and plasticity [35]. A more general way to arrive at the same result is to rejuvenate the glass structure and restore plasticity through cryogenic thermal cycling [17]. Cyclic cooling in liquid nitrogen increases the resistance to compression and extension through flexible deformation within nanoscale zones. In a way reminiscent of the thermal tempering of oxide glasses (Chapters 3.12 and 6.7), it results from the production of internal stresses through local differences in thermal expansion in heterogeneities of the atomic structure.

4.3 Fracture Toughness

The fracture toughness, i.e. the ability of a material to resist crack propagation and fracture, is also excellent for some metallic glasses. The invention of $\text{Pd}_{79}\text{Ag}_{3.5}\text{P}_6\text{Si}_{9.5}\text{Ge}_2$ glass with a fracture toughness up to 200 $\text{MPa}\sqrt{\text{m}}$ (though only a small size sample was tested) and a high damage tolerance was particularly instrumental to increase the scientific interest paid to these fascinating materials [36]. For compositions that vitrify readily, the availability of large enough samples has actually allowed accurate mechanical measurements to be performed without yielding the spuriously high values that could otherwise be obtained. Whereas the fracture toughness obtained on 7 mm thick fatigue pre-cracked tension specimen of the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ glass is 55 $\text{MPa}\sqrt{\text{m}}$ [37], heat treatment resulting in partial or full crystallization leads to a 50-fold reduction in K_{Ic} values to 1.21 and 1.04 $\text{MPa}\sqrt{\text{m}}$, respectively. Values of fracture toughness in the range 35–75 $\text{MPa}\sqrt{\text{m}}$ have been found in three-point bending tests for pre-cracked and notched $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ specimens [9].

4.4 Friction and Wear Resistance

Metallic glasses have also been investigated with respect to wear and friction under dry sliding conditions. Friction coefficients range from 0.30 to 0.45. The wear resistance of Zr-based glasses is about 5×10^{11} Pa whereas that of Fe-based glasses reaches about 5×10^{14} Pa and could be even higher for Co-based glasses [38]. Owing to their low elastic moduli, high specific strength and excellent processing characteristics in the supercooled liquid state, metallic glasses appear to be promising materials for

applications in micromechanical systems. Their tribology has thus also been studied at the nano and atomic scales.

4.5 Fatigue

The fatigue-endurance limits of some Zr-based glasses are comparable with those of high-strength crystalline alloys (Table 3) [39]. In video-resolved thermographies of mechanical damage in metallic glasses, one can observe thermoelastic and heat-transfer effects. In addition, a thermoelastic degradation attributed to free-volume accumulation is observed at the center of the specimen. But no shear bands (see Section 5.1) are observed before failure during these fatigue experiments. The crack-initiation mechanisms upon fatigue testing could thus be surface-voids and defects, and not the shear band of tensile testing.

4.6 Low-temperature Mechanical Properties

The maximum compressive stress of metallic glasses increases with decreasing testing temperatures [40]. For $\text{Zr}_{64.13}\text{Ni}_{10.12}\text{Cu}_{15.75}\text{Al}_{10}$, the yield stress under compression is, for instance, 1.8 and 2 GPa at room and liquid-nitrogen temperatures, respectively. This is reflected in acoustic-emission experiments in which the acoustic signal is significantly reduced at low temperatures [41], although localized shear bands are still formed (cf. Section 5.2). The transition from serrated to non-serrated plastic flow (see the following section) at liquid-nitrogen temperature thus suggests that the shear-band propagation velocity decreases because of the increased viscosity of the deforming regions.

5 Deformation Behavior at Room Temperature

5.1 Shear Transformation Zones

Although the majority of metallic glasses are brittle even under compression, some of them display a significantly higher compressive plasticity than others. Such an enhanced plasticity can be related to a high Poisson's ratio [42], an in-situ nanocrystallization, or a glass phase separation [9]. Also, it appears that embrittlement of Mg- and La-based alloys is caused by the inclusion of oxide particles of micron-size scale that act as stress concentrators because oxygen is soluble in solid Zr and Ti, but not in solid Mg and La [43].

A metallic glass thus begins to deform when a shear transformation zone forms near a stress concentrator, be it a flaw or a surface notch, which induces structural disordering. In the next step such zones unify in the form of a front that propagates as a shear band. At this stage, the strain within the band and the values of shear offset are rather small, causing small stress drops. A certain band can then gradually reach the opposite surface of the sample, leaving behind it either a relatively flat or a complex-shaped, curved 2-D interface. Between the two parts of the sample a friction-induced vibration manifests itself as a slip-stick process while further deformation takes place in this band as indicated by a change in the stress-strain curve. In other words, formation of new shear bands with relatively small shear offsets first prevails before deformation proceeds mainly through the existing dominant shear band(s) (Figure 11). These two types of deformation regimes may result in the bimodal distribution of the shear offsets observed earlier.

Table 3 Mechanical strength and fatigue data of bulk metallic glasses tested at 10 Hz frequency and the ratio of minimum to maximum stress of 0.1.

BMG	Tensile strength (MPa)	Geometry	Testing scheme	Fatigue limit (MPa)	Fatigue ratio
$\text{Zr}_{50}\text{Cu}_{37}\text{Al}_{10}\text{Pd}_3$	1900	Cylinder ^a	T	983	0.52
$\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Al}_{10}\text{Ni}_{14.6}\text{Ti}_5$	1700	Cylinder	T	907	0.53
$\text{Zr}_{50}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_{10}$	1900	Cylinder	T	865	0.46
$\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$	1820	Cylinder	T	752	0.41
$\text{Zr}_{41.2}\text{Cu}_{12.5}\text{Ni}_{10}\text{Ti}_{13.8}\text{Be}_{22.5}$	1850	Cylinder	T	615	0.33
$\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{Er}_2\text{C}_{15}\text{B}_6$	4200	Plate ^b	FPB	673	0.16
$\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$	1850	Plate	FPB	218	0.12

T, tensile test of notched sample; FPB, four-point bending.

^a 3 mm diameter.

^b 3 × 3 × 25 mm.

Source: Data from [39].

5.2 Shear Deformation Bands

At lower temperatures metallic glasses flow plastically in an inhomogeneous way through the formation and propagation of shear bands, which are 10–20 nm thick and manifest themselves as surface steps up to several micrometers in height. Because the process is considered to be stochastic, the dominant shear band that eventually forms does so at different strains in different samples. Experimentally, the formation of shear bands is revealed by wavy, or *serrated*, stress–strain curves, every small stress drop being caused by an individual event (the so-called Portevin–Le Chatelier effect). At room temperature, it is because of this dominant mode of plastic deformation that metallic glasses have no tensile ductility, except in the few special cases of thin sections of hypoeutectic alloys tested at relatively high strain rates. Other examples are Zr-based thin foils for which in-situ TEM observations have demonstrated the much higher ductility of hypo- compared with hypereutectic alloys, which originates in their larger excess volumes.

5.3 Shear Softening

Shear softening may result from local heating or be stress driven instead. In a shear band, however, friction in a liquid layer may alternatively act as a heat source. When the central zone of the shear band heats up at high strain rates through friction forces, its viscosity can decrease by several orders of magnitude and, thus, result in an increase of the shear speed. But at some point the band finds itself stopped, likely owing to an axial-stress decrease, until the next round of stress increase. Eventually, fracture suddenly takes place at a critical shear offset because of sudden viscosity reduction caused by the heat released through friction forces.

A change in the deformation stage is observed in metallic glassy samples [44]. In the plastic range, the strain curve of a typical 2 : 1 height to diameter ratio cylindrical $\text{Zr}_{62.5}\text{Cu}_{22.5}\text{Fe}_5\text{Al}_{10}$ sample subjected to continuous loading illustrates a change in deformation mechanisms observed in metallic glasses (Figure 11). From the beginning to the eventual fracture, plastic deformation proceeds discontinuously as indicated by the repeated stress drops observed. After about 2% of plastic deformation, the change observed in the magnitude distribution of the stress drops thus indicates a limit between two deformation regimes. In the first, new shear bands repeatedly form and propagate throughout the sample; the second one begins when they give rise to a major/dominant shear band, which later propagates in a stick–slip way.

Interestingly (Figure 12), cylindrical 1 : 2 samples can deform to large strains without forming such a dominant shear band because this aspect ratio makes it possible to keep a nearly homogeneous deformation at a

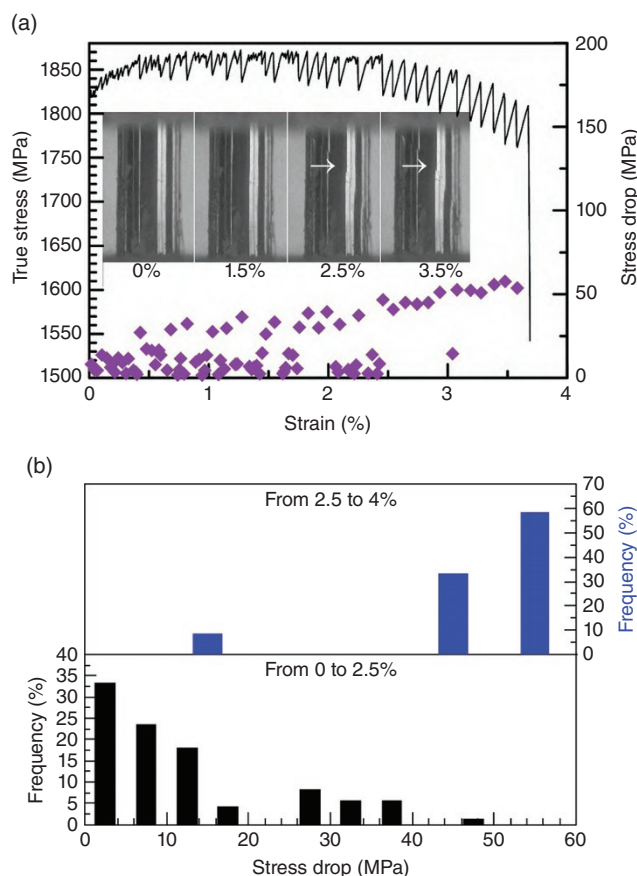


Figure 11 The wavy, or *serrated*, stress-deformation relationship of a 2 : 1 (height to diameter ratio) cylinder of the $\text{Zr}_{62.5}\text{Cu}_{22.5}\text{Fe}_5\text{Al}_{10}$ glass upon room-temperature compression. (a) Stress (top curve) and repeated stress drops (bottom, diamonds) causing the plastic deformation shown by the video snapshots from 0 up to 3.5%, at which fracture took place. (b) Frequency distribution of the magnitude of stress drops calculated from the continuous strain–stress curve in (a) in two ranges, namely, from 0 to 2.5% and from 2.5 to about 4%. Source: Reproduced from [44] with permission of Elsevier.

macroscopic scale [45]. From differential scanning calorimetry (DSC) thermograms of deformed samples (Figure 13), complementary information can be drawn in terms of T_g , T_x , and exothermic peak (T_p) temperatures, and of enthalpies of relaxation (ΔH_r), overshoot (ΔH_o), and crystallization (ΔH_c). The values of T_g and T_x decrease but ΔH_r and ΔH_o increase at 0.24 and 0.68 strain whereas other parameters are less affected.

Before crack initiation takes place at a larger strain, the formation of a great number of shear bands may thus have a twofold effect on the properties of a strongly deformed metallic glass. Locally, a higher energy state is reached (as in case of glassy phase rejuvenation), which is released after failure of the sample. The areas deformed either plastically (within the shear bands) or elastically (at the edges of not well-developed shear bands which did not propagate

Figure 12 Strain–stress curves of a 1:2 (height to diameter ratio) cylinder of the $\text{Zr}_{62.5}\text{Cu}_{22.5}\text{Fe}_5\text{Al}_{10}$ glass upon room-temperature compression. Derivative of the stress with respect of the strain included (right scale). Insets: (a) close-up of the curve between 0.10 and 0.12 strain. (b) Optical image of the initial sample and after deformation at 0.24, 0.68, and 0.80 strain, respectively, from left to right. Source: Reproduced from [45] with permission of Elsevier.

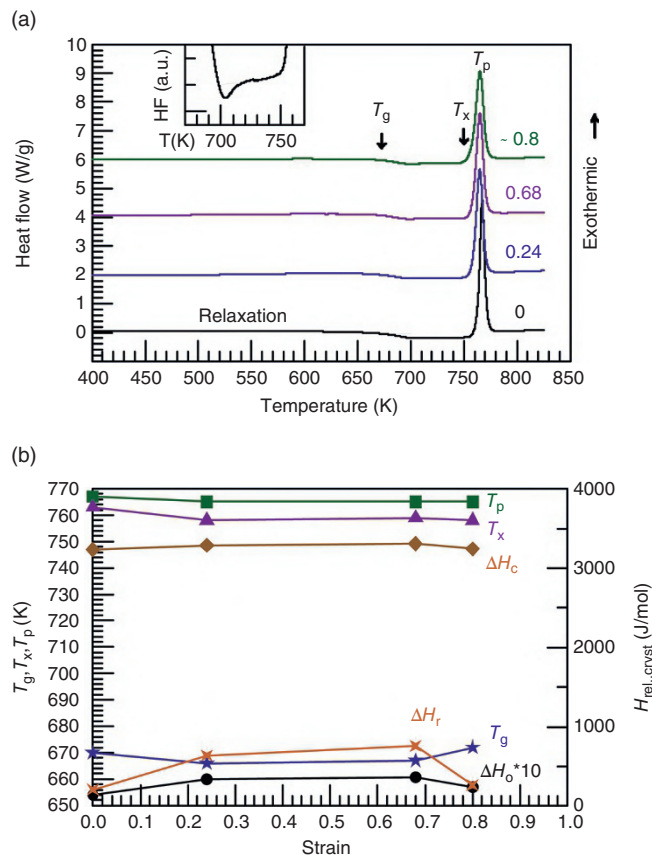
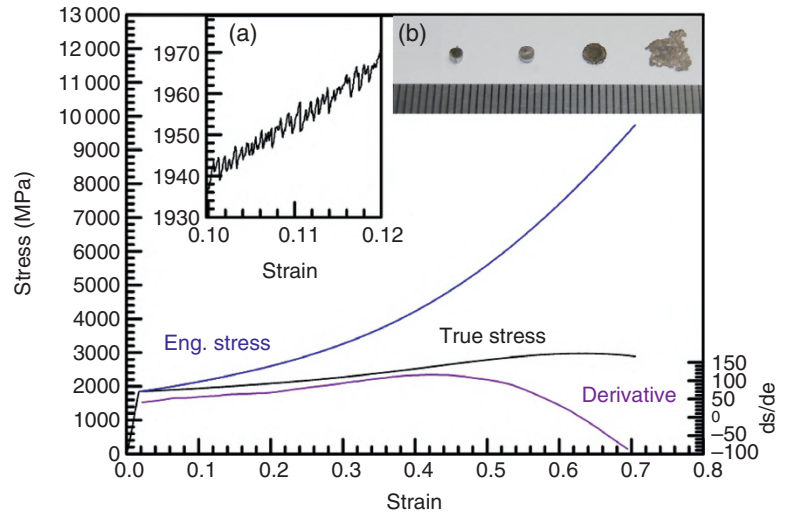


Figure 13 Thermal properties of the $\text{Zr}_{62.5}\text{Cu}_{22.5}\text{Fe}_5\text{Al}_{10}$ glass cylinders after room-temperature compression. (a) Differential scanning calorimetry thermograms of the studied alloys heated at 40 K/min. Inset: heat-flow overshoot after completion of the glass transition. (b) Characteristic temperatures and enthalpies of relaxation and crystallization derived from the thermograms. Source: Reproduced from [45] with permission of Elsevier.

till the other side of the sample) release a significant amount of extra heat upon structural relaxation whereas the lower T_x may indicate easier crystallization made possible by favorable sites for heterogeneous nucleation in locally deformed areas. On the other hand, another part of the glass matrix may suffer from the opposite effect of structural relaxation, leading to an overall lower T_g and a larger heat overshoot of the DSC signal after the glass transition, which is indicative of a more relaxed glass.

5.4 Dynamic Mechanical Properties

Dynamic mechanical properties characterize the resistance of a material to impact loading. For brittle materials, mechanical properties are significantly worse under dynamic than under quasi-static loading. At first glance (Figure 14), this dependence becomes particularly abrupt between 10^3 and 10^4 s^{-1} as illustrated by a Zr-based glass [46]. The difference between the two regimes is that formation of shear bands predominates under quasi-static conditions whereas, as shown by high-speed cinematography, an adiabatic mechanism takes over at higher rates.

The impact fracture energy and stress for the $\text{Zr}_{50}\text{Al}_{10}\text{Cu}_{30}\text{Ni}_5$ glass have been measured with a standard Charpy test on specimens with U-shaped notches [47]. The maximum stress and displacement at the impact fracture are 1615 MPa and 0.44 mm, respectively, and the impact fracture energy is 63 kJ/m². The impact fracture stress is close to the static tensile fracture strength in a wide strain rate range of 10^{-4} to 10^{-1} s^{-1} . However, it decreases rapidly at strain rates higher than about 10^3 s^{-1} . The fracture surface appearance changes from a vein pattern in the region near the U-shaped notch to an equiaxed dimple-like pattern in the inner region.

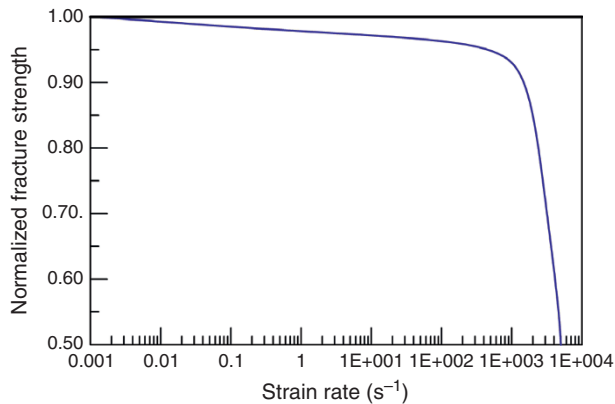


Figure 14 Schematic representation of strain-rate dependence of the fracture stress of a Zr-Ti-Cu-Ni-Al metallic glass.

5.5 Strain Rate Sensitivity

The strain rate sensitivity of polycrystalline alloys is generally positive, but negative for most metallic glasses under uniaxial compression [48]. The $\text{Zr}_{65}\text{Cu}_{20}\text{Fe}_5\text{Al}_{10}$ glass exhibits a negative sensitivity with a rate parameter m of -0.0026 calculated from the true stress-strain curves [9]. When indentation tests are made, however, an observed positive sensitivity parameter could be mainly attributed to a stress state that is close to those of three-axial compression tests. In this case not a single but several shear bands operate simultaneously.

5.6 Mechanical Behavior of Glass-Crystalline Composites

As seen in strain-stress diagrams, deformation changes leading to a greater plasticity can take place in metallic glasses that bear stress concentrators such as porous and dual crystal/glass materials. An interesting example is that of the dual-phase $\text{Ti}_{42.3}\text{Zr}_{7.7}\text{Cu}_{41.7}\text{Ni}_{7.3}\text{Co}_1$ with

1000 ppm of B where a crystalline $cP2$ phase is embedded in a glassy matrix. Multiple shear offsets are observed on the lateral surface of a compressed sample (Figure 15) [44]. Strain hardening, but hardly detectable serrated flow, was initially observed before small stress drops of 1–3.5 MPa took place after a plastic deformation of 4.5%. Eventually, the material fractured when strain-hardening mechanisms were exhausted in the crystal phase. Hence, the deformation of such a dual-phase material likely takes place through a series of small sample displacements in the shear bands although shear-banding mechanism remains active.

Microstructural toughening and ductility enhancement in metallic glasses and composites actually seem to be a fruitful way to engineer valuable structural and functional materials. The two basic principles involved are: (i) introduction of elastic/plastic inhomogeneities in a metallic glass matrix to initiate local shear banding around them; and (ii) matching of microstructural length scales to the characteristic length scale of crack opening to avoid crack development. Promising results have been obtained in this way on ductile $\text{La}_{86-y}\text{Al}_{14}(\text{Cu}, \text{Ni})_y$ samples with hcp α -La as a dendritic phase as well as on a variety of Zr-based glasses in which the dendritic phase is a body-centered cubic beta-type solid solution. In practice, however, the main problem currently met is that most of such ductile and tough materials made so far are based on expensive elements like Zr, Pt, and Pd.

5.7 Glassy-Crystal Alloys with Transformation-Induced Plasticity

Other structural transformations include deformation-induced crystallization, which can make metallic glasses more plastic. The extent of this plasticization is even more important if a crystal undergoes a phase transformation during deformation. The effect is then similar

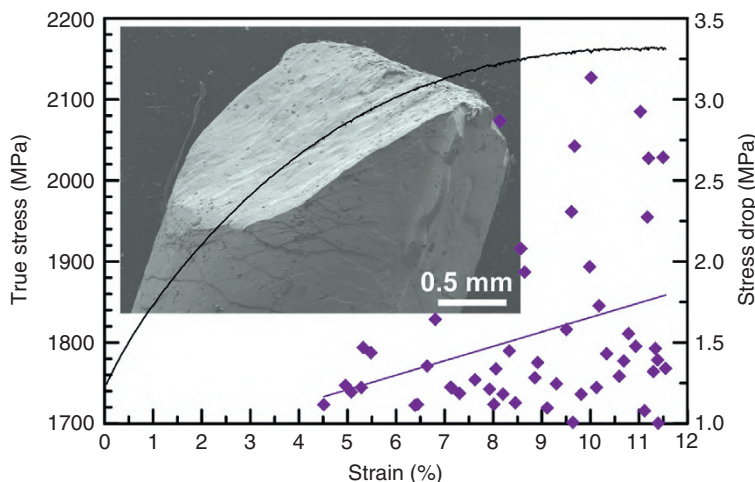


Figure 15 Stress and stress drops as a function of plastic strain for the cylindrical $\text{Ti}_{42.3}\text{Zr}_{7.7}\text{Cu}_{41.7}\text{Ni}_{7.3}\text{Co}_1$ crystal-glassy sample with 1000 ppm of B of 2 : 1 aspect ratio upon the compression test. The inset represents a lateral surface of the sample tested to fracture. The diamond symbols denote the stress drop values exceeding 1 MPa. Source: Reproduced from [44] with permission of Elsevier.

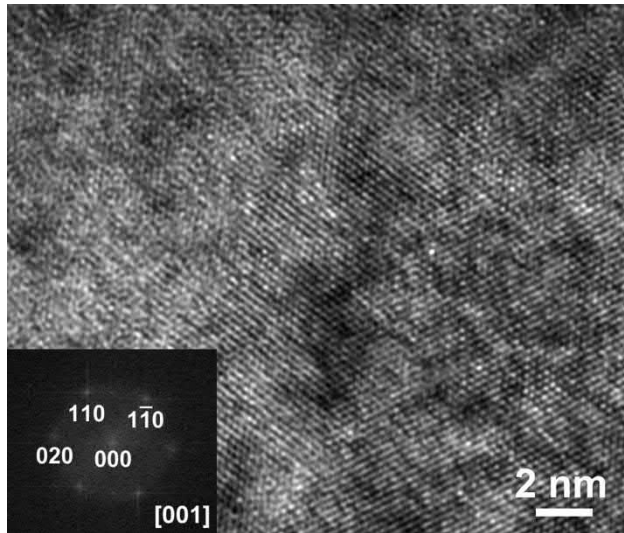


Figure 16 Boundary between the amorphous (left) and crystalline (right) phases after deformation of $\text{Ni}_{40}\text{Cu}_{10}\text{Ti}_{40}\text{Zr}_{10}$ glass as seen in by a high-resolution TEM micrograph. Inset: Fourier-transform pattern indexed according to the $mP4$ lattice of the TiNi phase.

to the transformation-induced plasticity (TRIP) of meta-stable austenitic steels and NiTi alloys [9]. The high strength and plasticity of amorphous $\text{Ni}_{40}\text{Cu}_{10}\text{Ti}_{33}\text{Zr}_{17}$ then result from the coexistence of its glass matrix with a $cP2$ ($B2$) crystalline phase analogous to that of austenitic NiTi. Various other composite materials based on Ni–Cu–Ti–Zr glasses have been produced by direct casting into a copper mold [49]. In some other similar composite materials, the martensitic transformation is reversible, leading to superelastic behavior. The structures of the as-cast materials contain a glassy matrix and a $cP2$ ($B2$) (Ni, Cu)(Ti, Zr) crystalline solid solution. Upon plastic deformation, this phase transforms to a $mP4$ ($B19'$) TiNi phase with a lower symmetry and a lamellar morphology (Figure 16). The combination of a hetero-phase structure with the dynamics of the deformation-induced martensitic transformation confers remarkably good strength and plasticity to the composite. The strain–stress relationship of the material (Figure 17) thus shows three different regimes: the deformation is first linearly elastic, then TRIP, and finally indicative of extensive shear- and slip-band formation.

6 Magnetism: Properties and Applications

6.1 Soft Magnetic Materials

Most metallic glasses are non-ferromagnetic but Fe-based glasses have attracted much interest because

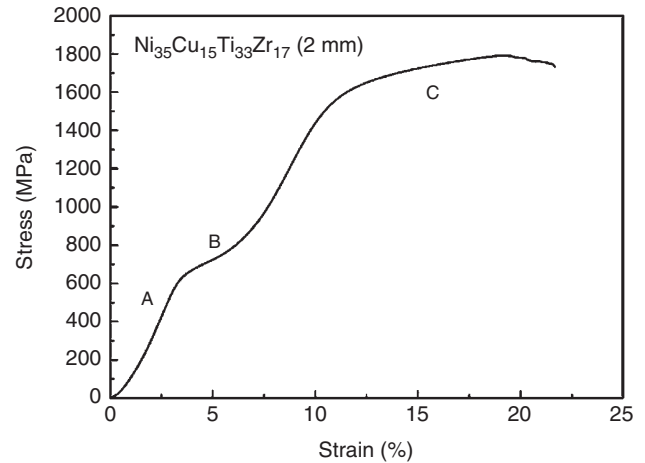


Figure 17 The three successive deformation regimes A, B, and C in the strain–stress relationship of the $\text{Ni}_{35}\text{Cu}_{15}\text{Ti}_{33}\text{Zr}_{17}$ alloy after elastic deformation.

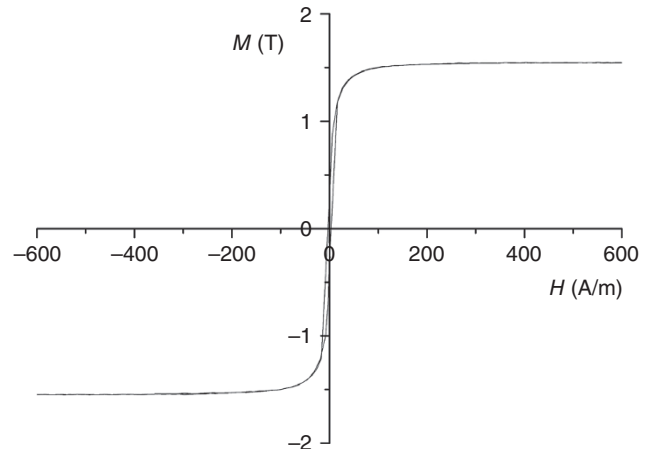


Figure 18 A typical magnetization curve of a Fe–Co-based metallic glass.

of the ease with which they can be magnetized and demagnetized. Although, magnetic alloys have long been limited to marginal glass-forming compositions *soft* magnetic properties are achieved in as-cast $\text{Fe}_{56}\text{Co}_7\text{Ni}_7\text{Nb}_{10}\text{B}_{20}$ bulk rod samples (Figure 18), whose coercivity is lower than 10^3 A/m. One of the most promising $\text{Fe}_{76}\text{Si}_9\text{B}_{10}\text{P}_5$ BMG alloy exhibits a saturation magnetization (M_s) of 1.51 T, a coercive force (H_c) of 0.8 A/m, and a critical diameter (D_{cr}) of 2.5 mm [50].

For soft magnetic crystalline materials, H_c increases with grain size (D) with a maximum at about 10^2 nm whereas coarse-grained and nanostructured alloys have lower H_c values. The formation of a nanostructure within a glassy phase thus improves its soft magnetic properties. For example, after annealing at 873 K for 30 seconds, the as-cast $\text{Fe}_{76.5}\text{C}_6\text{Si}_{3.3}\text{B}_{5.5}\text{P}_{8.7}$ glass displays a modified

medium-range order in 1–3 nm zones of its glassy matrix. As a result, the saturation magnetization and permeability (μ) are enhanced from 1.35 T and 3500 to 1.57 T and 9890, respectively, whereas the coercivity is lower than 20 A/m [51].

Compared to other glasses, the (Fe–Co)-based ones are also particularly attractive for engineering applications, thanks to their combination of ultrahigh strength, superior wear resistance, and good GFA with a critical diameter D_{cr} of 2.5 mm. The $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$ glass, for instance, exhibits an extremely low coercive force of 0.25 A/m along with a maximum permeability of 550 000. It also has a saturation magnetization of 1.51 T, a coercivity of 0.8 A/m.

Such soft ferromagnetic glasses are now widely used. Licalloy[®] designates those of the Fe–Cr–P–C–B–Si system produced by cold consolidation of atomized glass powders with resin [8]. The Licalloy cores exhibit nearly constant relative permeability in a wide frequency range extending up to several megahertz.

Other soft magnetic powder cores have been developed in cooperation with the NEC TOKIN Corporation from the Fe–Nb–B–Si, Fe–Nb–B–P, and Fe–Nb–B–Si–P systems. The new SENNTIX-II powder cores (Fe–Nb–Cr–B–P and Fe–Nb–Cr–B–P–Si systems) have further reduced core losses [8].

6.2 Hard Magnetic Materials

In contrast, Nd-based glasses show *hard* magnetic properties with a coercivity higher than about 10^4 A/m, which can be used as permanent magnets. Permanent magnets must have a large coercive force, an elevated saturation magnetization, and a high energy product (BH_{max}). The ferromagnetic remanence (B_r), the magnetization under a field of 1242 kA/m, and the coercive force of the bulk $\text{Nd}_{60}\text{Fe}_{30}\text{Al}_{10}$ glassy alloy are 0.110 T, 0.163 T, and 292 kA/m, respectively [52]. The maximum sample thickness for formation of amorphous phase is 6 mm. The $\text{Nd}_{70}\text{Fe}_{20}\text{Al}_{10}$ glass shows ferromagnetism with a Curie temperature T_c of about 600 K. These hard-magnetic properties are presumably due to the development of homogeneous ferromagnetic clusters with a large random magnetic anisotropy.

7 Other Properties and Applications

7.1 Structural and Functional

Other important applications of metallic glasses rely on their excellent mechanical and chemical properties combined with good formability in the supercooled liquid state. These glasses have a smooth surface and soften

on heating at about T_g , which allows the creation of micro and nanoscale patterns on their surfaces by molding. After cooling, the material becomes hard again and can be used as a stamp for others (Figure 19) [53]. Of great interest are also the high elastic-strain limit and fracture toughness ensured by the lack of dislocations and grain boundaries, which make it possible to miniaturize components especially in micro-electromechanical systems. A few examples will illustrate how use can be made of these various features.

Striking application are the 1.5-mm and then the 0.9-mm motor assembled from parts made with Zr–Cu–Al–Ni and Ni–Zr–Ti–Fe–Co–Cu glasses. The former is a three-stage motor whose torque is about 20 times higher than that of the 4-mm conventional vibration motor of cell phones. Likewise, gears made of Zr- and Ni-based glasses have lifetimes 34 and 313 times longer, respectively, than those made with usual tool steel. The micro-g geared motors are being tested for applications to micro-machines, precision optics, and advanced medical equipments such as endoscopes and micro-pumps.

Owing to its high tensile strength and large elastic strain, Ti-based glassy pipes of 2 mm in outer diameter are suitable as sensing elements in Coriolis flow meters used to for gases or liquids in pipes subjected to reinforced oscillations. The sensitivity of such a flow meter is 28–53 times higher than that of the conventional SUS316 pipe [8].

Metallic micro- and nano-wires have applications ranging from interconnectors to sensors. The diaphragms produced by net-shape casting of the Zr–Cu–Al–Ni glasses have been integrated in pressure sensors to achieve much smaller sizes, higher sensitivity, and pressure endurance than with stainless steel.

The AMO-beads[®] powders of the Fe–Ni–Cr–Mo–B–Si glass are used to produce shot-peening balls and fine, precise polishing media by the water atomization process whereby water jets are impinging a falling stream of liquid metal to produce small particles of metallic glass [8]. These balls have much longer endurance times compared with those made with cast-steel and high-speed steels. The AMO-beads are used as shot-peening balls for high-alloy steel to improve its fatigue strength by 50–80% and increase the residual stress on its surface to more than 2000 MPa. Another important advantage is an extremely high resistance to powder explosion reaction in air. Like Fe-based glasses with good soft magnetic properties, they are valuable for micro *mirror actuation*, i.e. extremely accurate positioning of optical components.

7.2 Chemical

Owing to chemically homogeneous composition, lack of grain boundaries and dislocations, metallic glasses with

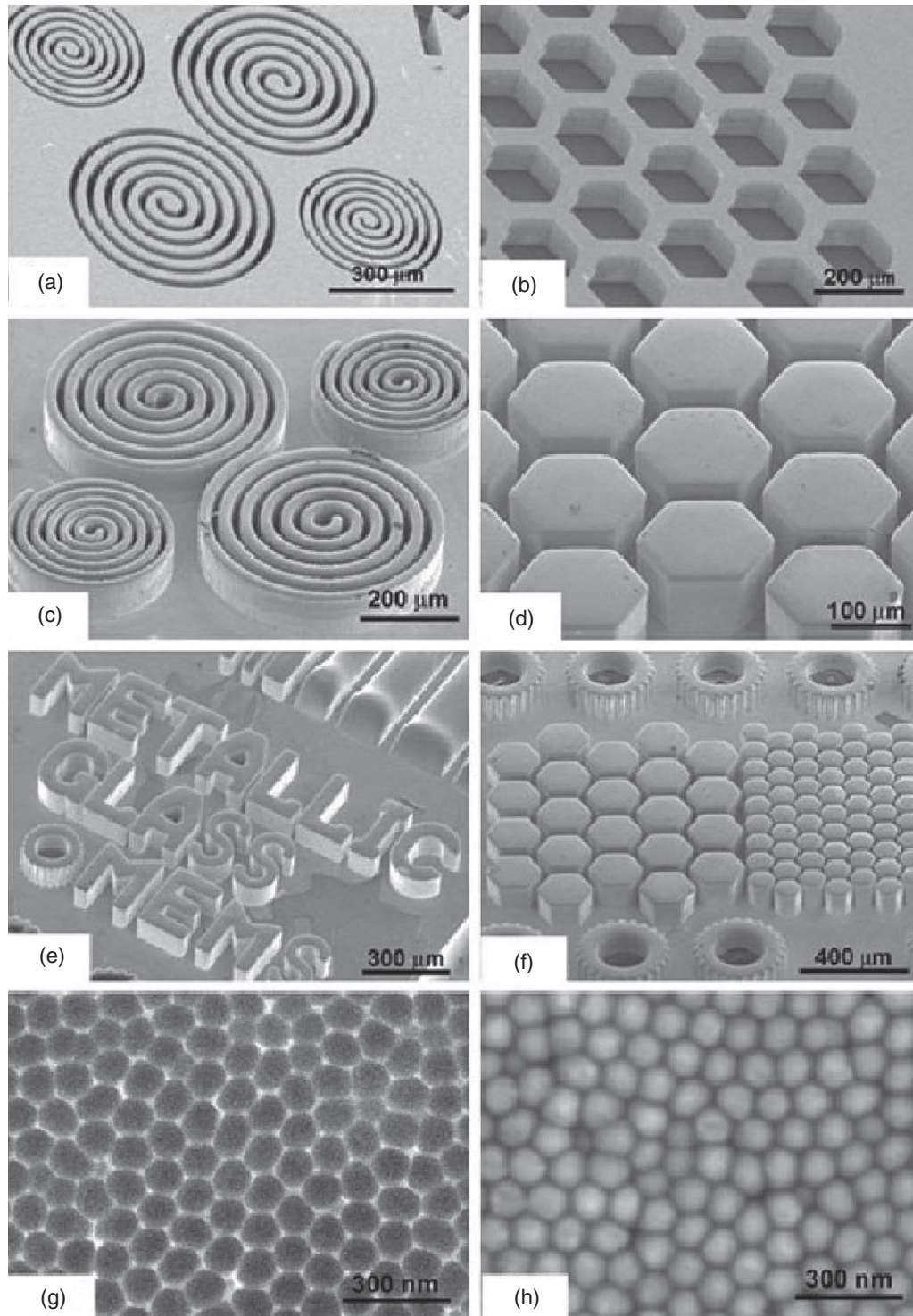


Figure 19 Scanning electron microscopy microphotographs: (a) and (b) are Si molds, (c–f) are the patterns fabricated with Si molds, (g) is porous alumina, and (h) is the corresponding nanorods fabricated with the porous alumina (g). All the above structures are obtained using molding with the $\text{Pd}_{40}\text{Ni}_{40}\text{Si}_4\text{P}_{16}$ glassy ribbons. Source: Reprinted from [53] with permission of Springer.

spontaneous passivation and low passive current densities have a high resistance against pitting corrosion. In Cr-bearing glasses, this property is, for instance, enhanced by the formation of Cr-rich passive films upon immersion in 1 or 6 N HCl solutions. The corrosion rates of the $\text{Fe}_{50-x}\text{Cr}_{16}\text{Mo}_{16}\text{C}_{18}\text{B}_x$ glasses are within 10^{-3} – 10^{-2} mm/year in 1, 6, and 12 N HCl solutions, respectively. Pitting corrosion does not even take place in a 12 N HCl solution up to a potential of 1.0 V (Ag/AgCl) [54].

Likewise, the passive current densities of the $(\text{Ti}_{0.45}\text{Zr}_{0.1}\text{Pd}_{0.1}\text{Cu}_{0.31}\text{Sn}_{0.4})_{98}\text{Nb}_2$ glass are about 10^{-3} A/m² in phosphate-buffered saline solution. The values of less than 10^{-2} A/m² in lactic acid, and of 10^{-2} A/m² in Hank's solution, are thus lower than those of pure Ti metal, Ti–6Al–4V alloy [55]. The high corrosion resistance of some metallic glasses makes them exceptionally useful for chemical vessels.

Nanostructured metallic glasses represent a new class of materials synthesized from dense packing of nanometer-sized glassy particles (Figure 20). New application in the field of catalysis are opened by Au-based metallic nanoglasses with large surface areas [56]. A good activity has, for instance, been obtained for the reaction of dimethylphenylsilane $[(\text{CH}_3)_2\text{C}_6\text{H}_5\text{SiH}]$ with water to produce the desired dimethylphenylsilanol $[(\text{CH}_3)_2\text{C}_6\text{H}_5\text{SiOH}]$ in 24 hours at room temperature. Another useful chemical application is the degradation of organic pollutants in water like *azo dyes*. The $\text{C}_{32}\text{H}_{20}\text{N}_6\text{Na}_4\text{O}_{14}\text{S}_4$ dye is completely decomposed in an aqueous solution by $\text{Fe}_{73}\text{Si}_7\text{B}_{17}\text{Nb}_3$ metallic glass powders about 200 times faster than with crystalline Fe powders although the glass contains chemically inactive metalloid elements [57].

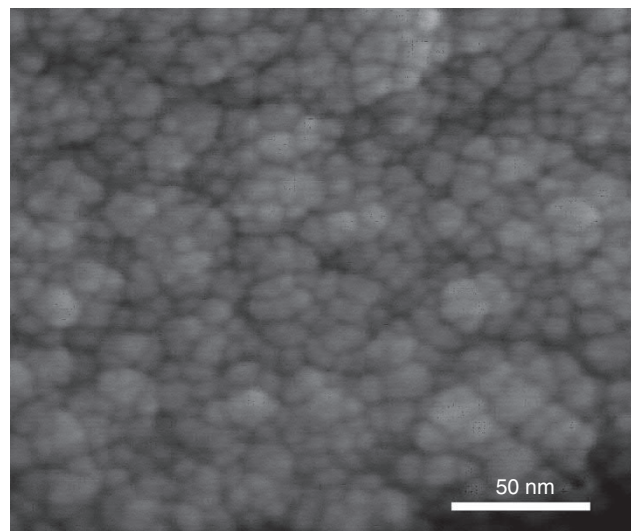


Figure 20 The structure of a Zr–Pd metallic nanoglass studied by scanning electron microscopy.

7.3 Medical

Two types of medical implant materials have been made from metallic glasses: (i) chemically and biologically inert materials that are not soluble in the human body owing to their high corrosion resistance; for example, glasses of the Ti–Zr–Pd–Cu–Sn–Nb system [55]; and (ii) biodegradable materials consisting of body-friendly metals which dissolve with time so that they do not need to be removed after an operation as exemplified by glasses of the Mg–Zn–Ca ($\text{Mg}_{60}\text{Zn}_{35}\text{Ca}_5$) [58] and Ca–Mg–Zn ($\text{Ca}_{65}\text{Mg}_{15}\text{Zn}_{20}$) systems [59]. The $\text{Ca}_{65}\text{Li}_{6.46}\text{Mg}_{5.54}\text{Zn}_{23}$, $\text{Ca}_{65}\text{Li}_{7.54}\text{Mg}_{6.46}\text{Zn}_{21}$, $\text{Ca}_{65}\text{Li}_{9.96}\text{Mg}_{8.54}\text{Zn}_{16.5}$, and $\text{Ca}_{65}\text{Li}_{14.54}\text{Mg}_{12.46}\text{Zn}_8$ are very light and have good thermoplastic formability close to room temperature but degrade rapidly [60]. Porous metallic glasses can also be used as bio-implants (Chapter 8.4) or damping materials owing to their reduced Young's modulus compared with monolithic metallic glasses.

8 Perspectives

Initially the high cost of elements like gold and palladium seriously hindered practical applications of bulk metallic glasses. The situation thus completely changed when other glasses based on “industrial” metals such as iron, copper, magnesium, and titanium were produced and much bigger pieces progressively obtained (Figure 21). Since then engineers have taken advantage in a great many ways of the strength, hardness, wear resistance, large elastic deformation, and high resistance to corrosion of the new glass families.

From a physical standpoint, Fe-based glasses with good soft magnetic properties are valuable for *mirror actuation*, i.e. extremely accurate positioning of optical components. On the chemical side, Zr–Hf–Ni and Ni–Nb–Zr glasses have a high hydrogen solubility and significant resistance to embrittlement, which make them promising for hydrogen-permeation applications in separators for fuel cells and other membranes. As for nanoglasses, they show unique properties, including enhanced catalytic activity as well as good biological and mechanical properties compared with their homogeneous glass counterparts.



Figure 21 A bulk metallic glass piece: a 5-cm long Zr–Cu–Fe–Al alloy rod.

On the other hand, many questions remain to be solved from a theoretical standpoint. The glass transition has been studied extensively in metallic glasses, but there is still no general agreement on its nature, for instance, on whether it is a purely kinetic or thermodynamic phase transformation. Although equilibrium liquids are homogeneous at a laboratory timescale, there are reasons to believe that deeply supercooled liquids, and the glasses that inherit their structure, are rather heterogeneous in terms of their dynamics. Such heterogeneities in glasses are and will be widely discussed especially in relation to the composition–structure–microstructure relationships, which need to be understood better, for instance, to increase the plasticity and the impact fracture toughness of these materials.

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7.11

Glass-Ceramics

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1 Introduction

Glass-ceramics are materials that are first melted and shaped as glass articles and then partially crystallized upon further heat treatment. Depending on the composition of the initial glass, the nature of the crystals formed, and the heat treatments applied, the microstructure of the material can be tailored to specific needs and a wide range of original properties can be obtained. As compared, with vitrification only, crystallization thus opens a large number of possibilities and allows materials with unusual properties to be developed. If glass-ceramics have encountered great commercial success, it is, therefore, because they display a combination of specific properties difficult or impossible to obtain with either a glass or a ceramic.

The best-known products are the low-expansion, transparent glass-ceramics made with lithium aluminosilicates whose applications range from consumer products such as cooktop panels to telescope mirrors. However, other glass-ceramics, such as those based on lithium silicates, display outstanding mechanical strength and good translucency and are used as dental materials. Similarly, glass-ceramics based on micas can be machinable; these are unique and difficult to replace with other materials.

From the research point of view, crystallization remains an intriguing topic. Ever since their discovery in the 1950s, glass-ceramics have been subjected to many fundamental and applied studies in fields such as nucleation and crystallization mechanisms, microstructure, microstructure-properties relationships, and product development in a variety of glass systems. The purpose of this chapter is to review these advances. We will begin with

the history of glass-ceramics and then describe their present uses, processes of production, and main properties. The main composition systems will finally be reviewed.

Even though glass-ceramics are mainly made up of silicates, materials have been developed from other systems. In addition to phosphates, which are dealt with in this chapter, chalcogenides are noteworthy: some of them retain the high transmission in the infrared range of the precursor glasses but display improved thermomechanical properties [1].

2 History and Present Uses of Glass-Ceramics

Because glass is thermodynamically metastable with respect to an isochemical crystalline assemblage (Chapter 5.3), a long-standing problem faced by glass-makers throughout the ages was to avoid partial crystallization when blowing or forming by other means the glass product at temperatures at which the crystallization kinetics may be significant. Partial crystallization thus remained a transformation to be prevented from happening until the physicist and naturalist René-Antoine Ferchault de Réaumur (1683–1757) made and marketed a kind of “China” by crystallizing plain glass bottles upon long annealing in sand ([2], Chapter 10.11). Even though Réaumur’s products were nicely looking and resistant to thermal shock, production had to be discontinued because of low mechanical strength that was itself due to the fact that crystallization was initiated at the surface and ended up being inhomogeneous in the bulk.

Work made much later in Germany by Gustav Tamman (1868–1938) showed that crystallization actually takes place in two different steps of nucleation and crystal growth (Chapter 5.4). Nucleation appeared difficult to

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control, however, because it generally takes place preferentially either at the glass surface or in the bulk when defects such as bubbles and batch stones are present. Between 1920 and 1950, glass crystallization via volume nucleation was much studied but the products obtained were difficult to form because the glass tended to crystallize upon cooling in a way that was difficult to control [3].

The process yielding fine-grained crystallization from volume nucleation was serendipitously discovered in the mid-1950s by S. D. Stookey, a Corning researcher, who was studying photosensitive glasses made of lithium silicates doped with low amounts of silver [4]. One night, a thermal treatment of these glasses went wrong when the furnace temperature, which was set at 450 °C, accidentally reached 850 °C. The following morning, Stookey was surprised to discover that, despite this high temperature, the glass had not sagged and did not break when it accidentally fell on the floor. Further analysis revealed that it had crystallized from the nucleating sites provided by the silver colloids dispersed in the volume. Thanks to this experiment, Stookey realized that many glasses could transform into glass-ceramics whose properties would depend on the nature of the crystals formed. This transformation generally requires the presence of appropriate nucleating agents, i.e. of elements that are soluble in the melt at high temperature but precipitate as a multitude of tiny crystals upon cooling and serve as nucleating sites for crystallization of the intended phases.

By the end of the 1950s, Stookey's discovery had led to the development and commercialization of new products by Corning [5]: Fotoform[®] and Fotoceram[®], chemically machinable lithium silicate materials; Code 9606, a glass-ceramic based on cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) used to produce radomes for the aerospace industry (Figure 1); and Corning Ware[®], a material containing the low thermal-expansion phase spodumene ($\text{LiAlSi}_2\text{O}_6$) employed as cooking ware.

Thereafter, research has aimed at increasing mechanical strength and obtaining low thermal-expansion and transparent glass-ceramics [5]. The former effort has led to the development of machinable glass-ceramics and of materials displaying outstanding strength and toughness that resulted from their particular microstructures; an example is Pyroceram[®] tableware. The first transparent products were Schott's Zerodur[®] launched in 1968 (a glass-ceramic with a very low thermal expansion produced for space applications, especially telescope mirrors) and Vision[®] cookware. Beginning in the 1980s, cooktops and fire-resistant windows were subsequently developed. Since then, the diversity of applications has kept growing and the products made of glass-ceramics may be grouped as follows in terms of uses [6, 7]:



Figure 1 Code 9606 glass-ceramic, containing cordierite as main crystalline phase, used as radomes in the aerospace industry (Corning). The height of the pieces range from 0.3 to 1 m.

- Optical applications (telescope mirrors, photonics)
- Consumer applications (cooktops, cookware, etc.)
- Medical applications (bone prostheses, dental restorations)
- Architectural applications (building materials, fire-resistant windows)
- Electronic applications (substrates for electronic packaging, memory disks)
- Energy applications (for example, high ionic-conductivity materials, which could be used as electrolytes)
- Defense applications (for example, transparent armors)
- Technical applications (radomes, machinable materials, and sealing materials)

To illustrate this range of glass-ceramics, representative compositions of commercial materials are listed in Table 1 and their main properties are summarized in Table 2. To complement this picture, the compositions and properties of a few other materials are presented in Table 3, and Table 4 gives the chemical formulas of the main phases mentioned in this chapter.

There are many producers of glass-ceramics. Some are glass companies making specialty glasses (Corning, Schott, Nippon Electric Glass, Ohara, etc.), whereas others specialize in one business (i.e. Ivoclar Vivadent for dental restoration, Eurokera for cooktop). Although glass-ceramics are not widely employed in energy- or environment-related fields, research is very active in these

Table 1 Representative compositions of a few commercial glass-ceramics [6].

	LAS glass-ceramics	Machinable glass-ceramics	Photosensitive glass and glass-ceramics	High-strength lithium disilicate glass-ceramics	Cordierite glass-ceramics
wt %	Typical range	Representative composition	Typical range	Typical range	Representative composition
SiO ₂	55–70	47.2	75–85	64–73	56.2
Al ₂ O ₃	15–27	16.7	3–6	0.5–5	19.8
B ₂ O ₃		8.5			
Li ₂ O	2–7		7–11	13–17	
MgO	0–4	14.5			14.7
ZnO	0–4		0–2		
TiO ₂	0–4				8.9
ZrO ₂	0–3			0–4	
K ₂ O	0–1	9.5	3–6	2–5	
Na ₂ O	0–1		1–2		
F		6.3			
Sb ₂ O ₃			0.2–0.4		
Ag ₂ O			0.05–0.15		
CeO ₂			0.01–0.04		
Others	Coloring agents, fining agents: 0–5			Nucleating agent: P ₂ O ₅	Fining agent

areas as demonstrated by an abundant literature and numerous patents. Glass-ceramics might, for instance, be used as substrates for solar cells, cathodes for lithium batteries, high-temperature seals for solid-oxide fuel cells, or immobilization of nuclear, industrial, or even municipal waste (Chapters 9.4, 9.5, 9.10, 9.11).

2.1 Formation of Glass-Ceramics

The development of glass-ceramics has long been made on an empirical basis. The detailed mechanisms of crystallization were not known, particularly the first nucleation step, which is either homogeneous or heterogeneous (Chapter 5.4). But much progress has been made recently [9, 10] through theoretical advances, which have concerned glass structure and related topics, and through the variety of analyses made possible by methods such as X-ray diffraction (XRD) and absorption, transmission electron microscopy (TEM), or nuclear magnetic resonance (NMR) (Chapters 3.1 and 3.2).

Homogeneous nucleation is rarely observed in glasses of practical interest. It occurs in phase-separated systems when one of the phases possesses a composition and a viscosity promoting crystallization [6].

An example is mullite ($2\text{SiO}_2-3\text{Al}_2\text{O}_3$), which crystallizes in aluminosilicate glasses: glass droplets of less than 100 nm and enriched in aluminum first form in the glass

matrix, and then crystallize as mullite to yield a transparent material.

Regarding heterogeneous nucleation, two different methods are possible depending on whether the process begins at the surface or in the bulk of the material (Figure 2). Heterogeneous nucleation most simply takes place at the surface of glass frits employed as starting products. With conventional ceramic technologies, a binder is added to the frit to make a paste, which is then shaped to the desired form. Whereas the binder is eliminated by thermal treatment, a further increase in temperature promotes sintering and then surface crystallization. To obtain a nonporous material, sintering must be achieved before the onset of crystal growth, because the presence of crystals increases the material viscosity and prevents sintering [11]. This technique is used to make a variety of products among which cordierite glass-ceramics are used as substrates in electronics, sealing materials, and building materials. An example is the Neoparies[®] glass-ceramic (sold by Nippon Electric Glass), with wollastonite as the main crystalline phase, for which a mix of different glass frits can give a marble aspect to the material.

For triggering bulk crystallization, nucleating agents are generally added to the base glass composition (Figure 2). They are soluble in the molten phase first produced, but not at lower temperatures. On cooling or at the beginning of further thermal treatment, they precipitate as crystallites uniformly distributed in the glass.

Table 2 Properties of a few commercial glass-ceramics.

	Macor glass-ceramic	Foturan [®] glass	Foturan [®] glass-ceramic	Lithium disilicate glass-ceramic (IPS e.max [®])	Code 9606	Zerodur [®] glass-ceramic	KeraBlack [®] Plus glass-ceramic	KeraWhite [®] glass-ceramic	LICGC™
Microstructure									
Main crystalline phase	Fluorophlogopite mica $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$	—	Lithium disilicate $\text{Li}_2\text{Si}_2\text{O}_5$	Lithium disilicate $\text{Li}_2\text{Si}_2\text{O}_5$	Cordierite $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	β -quartz solid solution	β -quartz solid solution	β -spodumene solid solution	Nasicon solid solution
Mean size of the crystals		—					≈ 40 nm	1 μm	
Amount of crystals	55 vol %	—	>60 vol %	>60 vol %			>70 vol %	> 70 vol %	
Thermal properties									
CTE ($\times 10^{-6} \text{ K}^{-1}$)	12 (20–800 °C)	8.5 (20–300 °C)	8.6 (20–300 °C)	10.6 (100–400 °C)	5.7 (25–300 °C)	0 $\pm$ 0.02 (0–100 °C)	0 $\pm$ 1 (25–700 °C)	1 (25–700 °C)	94 (30–350 °C)
Thermal conductivity (W/mK)	1.46 (25 °C)	1.35 (20 °C)	2.73 (20 °C)		3.71 (25 °C)	1.46 (20 °C)			
Continuous operating temperature	800 °C	400 °C	700 °C						
Resistance to thermal shocks and thermal gradients							$\Delta T_{\text{max}} = 700$ °C	$\Delta T_{\text{max}} = 650$ °C	
Mechanical properties									
Density (g/cm^3)	2.52	2.37	2.41		2.6		2.55	2.51	3.05
Young's modulus (GPa)	67	78	88		119	90	92	84	
Knoop hardness (100 g)	250				698	620 (0.1/20 ISO 9385)	600	658	590
Fracture toughness K_{IC}^a ($\text{MPa}\cdot\text{m}^{0.5}$)	1.53			2.3–2.9				0.95	
Flexural strength ^a (MPa)				400–610 ^b		110	≥ 150	≥ 110	
Electrical properties (room temp.)									
DC volume resistivity, ($\Omega \text{ cm}$)	10^{17}	8×10^{12}	6×10^{16}				6.3×10^6 (250 °C)	2.5×10^7 (250 °C)	
Dielectric strength (AC) (kV/mm)	45 (under 0.03 mm)				13.8 (under 0.002 mm)				
Dielectric constant	5.64 (8.5 GHz)	6.5 (1 MHz)	5.7 (1 MHz)		5.5 (8.5 GHz)		7.9 (1 MHz)	6.5 (1 MHz)	
Ionic conductivity (S/cm)-room temperature									1×10^{-4}

^a Fracture toughness and flexural strength only indicative as they much depend on the measurement method.

^b Biaxial flexural strength (ISO dental standard 6872).

Table 3 Composition and properties of a few noncommercial glass-ceramics.

	Transparent spinel glass-ceramic	Refractory glass-ceramic	Canasite glass-ceramic
Reference	GC1 [8]	[6]	[6]
Oxide (wt %)			
SiO ₂	58.3	34.1	57
Al ₂ O ₃	20.2	32.9	2
B ₂ O ₃			
Li ₂ O			
MgO	4.2		
CaO			11
ZnO	8.4		
SrO		23.9	
TiO ₂	3	9.1	
ZrO ₂	5		
Na ₂ O			8
K ₂ O			9
CaF ₂			13
Others (coloring agents, fining agents)			
Microstructure			
Main crystalline phase	Spinel	Sr-feldspar and Tielite	Canasite
Mean size of the crystals	~ 10 nm		length: 10–25 μm (lathlike)
Amount of crystals	~30 vol %		
Thermal properties			
CTE ($\times 10^{-6} \text{ K}^{-1}$)	$0.4 \times 10^{-6} \text{ K}^{-1}$	$0.4 \times 10^{-6} \text{ K}^{-1}$	
Strain point	945 °C		
Thermal conductivity (W/mK)			
Continuous operating temperature		1450 °C	
Mechanical properties			
Density (g/cm ³)	2.75	3.04	
Young's modulus (GPa)	98		82
Knoop hardness (100 g)	650		
Fracture toughness K_{IC} (MPa.m ^{0.5})		2.7 ± 0.2	4.8–5.2
Flexural strength (MPa)			300 (abraded)

Table 4 Chemical formula of the main crystalline phases mentioned in this chapter.

Name	Formula	Structure
Apatite	Ca ₁₀ (PO ₄) ₆ (O, F) ₂	
Cordierite	Mg ₂ Al ₄ Si ₅ O ₁₈	Ring silicate
β-Eucryptite	LiAlSiO ₄	Framework silicate
Fluoro-canasite	K ₂ Na ₄ Ca ₅ Si ₁₂ O ₃₀ F ₄	Chain silicate
Fluorphlogopite	KMg ₃ AlSi ₃ O ₁₀ F ₂	Sheet silicate
Lithium metasilicate	Li ₂ SiO ₃	
Lithium disilicate	Li ₂ Si ₂ O ₅	Sheet silicate
Mullite	3Al ₂ O ₃ ·2SiO ₂	
Spodumene	LiAlSi ₂ O ₆	Framework silicate
Spodumene solid solution	Li ₂ O·Al ₂ O ₃ · <i>n</i> SiO ₂ <i>n</i> = 4–10	Framework silicate
β-Quartz	SiO ₂	Framework silicate
β-Quartz solid solution	Li _{2-2(x+y)} Mg _x Zn _y O·Al ₂ O ₃ · <i>n</i> SiO ₂ <i>n</i> = 2–10	Framework silicate
Wollastonite	CaSiO ₃	Chain silicate

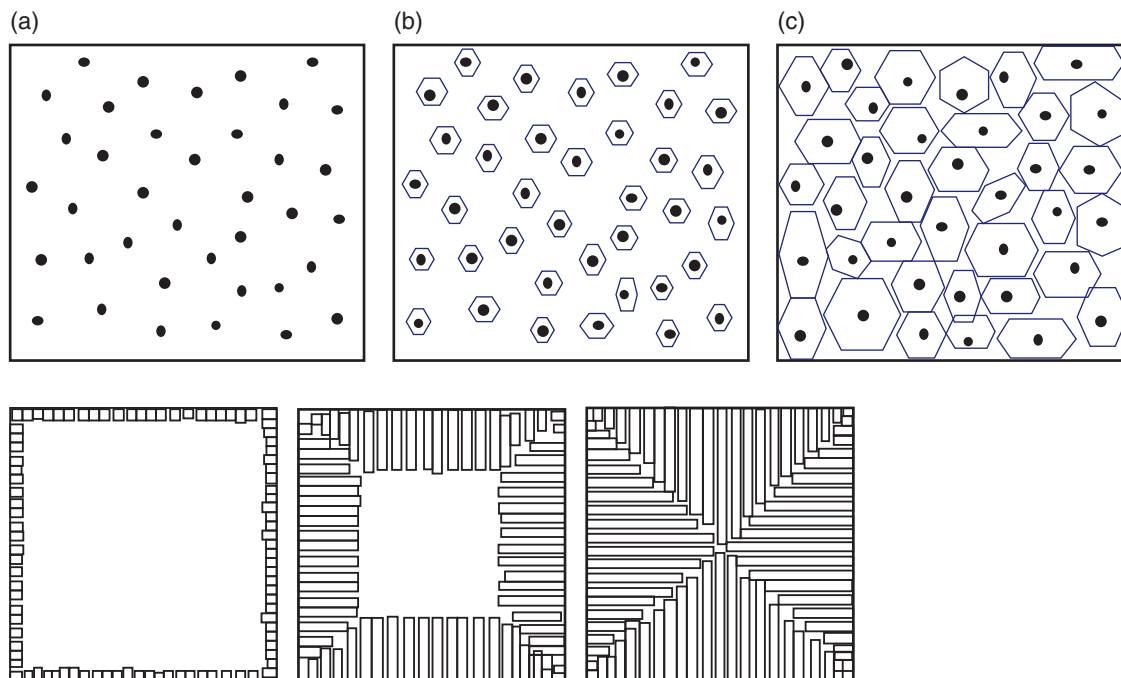


Figure 2 The two limiting case of crystal growth in glass [6]. Top: homogeneous nucleation in the bulk (a), followed by the nucleation and growth of the intended crystals on the nuclei (b) to yield the desired microstructure (c). Bottom: heterogeneous nucleation at the glass surface and subsequent inward crystal growth.

These crystallites serve as nucleation sites for the main crystalline phase(s). As described for homogeneous nucleation, liquid–liquid unmixing often plays a role: the nucleating agents can favor unmixing. Further crystallization, either of the nucleating phase or of the main crystalline phases, can then take place in one of the separated phase or begin from the interface.

In every glass system, only a limited number of efficient nucleating agents are available to promote precipitation of the intended crystals. For silicate glasses, these agents can be grouped into three families:

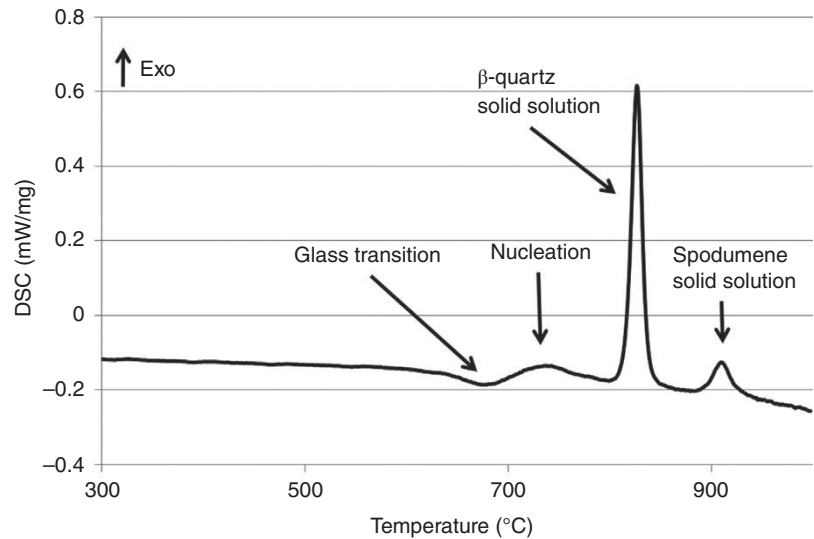
- 1) Oxides such as TiO_2 or ZrO_2 , which are efficient in aluminosilicate systems. They are added in the batch in typical amounts of 2–8 mol %. The crystallites that form include ZrO_2 or ZrTiO_4 in lithium aluminosilicate glass and $(\text{Mg}, \text{Al})(\text{Ti}, \text{Al})_2\text{O}_5$ pseudobrookite in magnesium aluminosilicate glass.
- 2) Fluorine, added as 2–8 mol % fluoride, allows phases containing this element (e.g. fluorides, apatites, micas, or amphiboles) to crystallize in a wide variety of silicate and aluminosilicate systems. The sequence of crystallization is generally complex. A preliminary step of liquid–liquid unmixing is often observed. It is followed by the crystallization of fluorides such as MgF_2 and CaF_2 and then of more complex phases.
- 3) Colloids of noble metals such as Ag, Pt, and Au, which can promote the crystallization of lithium, sodium, or

barium silicates. The metals are generally introduced in ionic form in amounts lower than 1 mol %.

After nucleation, the growth of the main crystal phase (s) is seldom a simple process because, in view of the generally incongruent nature of crystallization, crystal growth requires significant atomic diffusion from the bulk of the glass to the growing crystals, a problem that is compounded when several phases precipitate successively. Another complexity results from the markedly irreversible nature of crystallization at high degrees of supercooling, which tends to cause the precipitation of nonstoichiometric and structurally disordered crystals [12]. A last factor to be considered is metastability that can cause the transformation of the first crystals formed in another phase at higher temperature. A well-known example is the β -quartz solid solution, with which transparent and zero-expansion materials are obtained in the lithium aluminosilicate system, but which transforms to stable spodumene on further annealing above 950 °C. This crystallization sequence is clearly revealed by differential scanning calorimetry experiments (Figure 3).

Industrially, glass-ceramics are manufactured with conventional glass-forming techniques, for example, pressing for cookware, rolling for cooktops, or spin-casting for telescope mirrors. For silicates, appropriate nucleation rates are usually obtained from 50 to 100 K above the standard glass-transition temperature of the starting glass, whereas

Figure 3 Crystal nucleation and growth in a lithium aluminosilicate glass as indicated by the exothermic peaks observed near 740, 825, and 910 °C in a differential scanning calorimetry thermogram recorded on heating at a rate of 5 K/min.



crystal growth takes place at temperatures from 100 to 200 K higher. These two processes thus define two stages in the thermal treatment. The total duration of the thermal treatment can range from a few hours to several months, depending on the kinetics of nucleation and crystallization, and on the size of the pieces.

The processing of Zerodur to obtain telescope mirrors is especially notable in this respect [13] because the challenge is to satisfy tight dimensional requirements for very large pieces with excellent optical quality and uniform zero thermal expansion. For monolithic mirror substrates, the spin-casting process can produce a parabolic shape close to the final concave surface. The maximum size achieved has been 8 m in diameter and required 70 tons of molten glass. In this case, the cooling of the glass lasted three months and the ceramming process more than one year.

3 Properties of Glass-Ceramics

3.1 Microstructure

Glass-ceramics are essentially free of pores. Their properties strongly depend on their microstructure, which, regardless of the nucleation mechanism involved, is constituted of crystals homogeneously distributed in a residual glassy phase [6]. This microstructure can vary widely since these crystals can present different morphologies such as acicular, dendritic, and spherical, whereas their fraction typically ranges from 20 to 90 vol % and their size from 10 nm to a few microns (Figure 4).

3.2 Mechanical Properties

Glass-ceramics are fragile materials as glasses although the presence of crystals can impede crack propagation. Depending on their microstructure, very different

mechanical properties are in fact obtained [5, 6]. Glass-ceramics containing β -quartz solid solutions as the main crystalline phase display a mechanical strength close to that of the parent glass because the crystals have a small size of about 30 nm. On the other hand, some glass-ceramics containing lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) as the main crystalline phase present a toughness (K_{IC}) in the 2.3–2.9 $\text{MPa}\cdot\text{m}^{0.5}$ range and a modulus of rupture in the 400–610 MPa range. These high values result from the interlocking microstructure of the disilicate crystals. They are at the basis of the use of these materials in dental restoration.

Glass-ceramics containing the fluoro-canasil chain silicate $[(\text{Na}, \text{K})_6\text{Ca}_5\text{Si}_{12}\text{O}_{30}\text{F}_4]$ as main crystalline phase also display an outstanding mechanical strength (Table 3) since a K_{IC} of 5 $\text{MPa}\cdot\text{m}^{0.5}$ and a modulus of rupture of 300 MPa have been reported. Here again the microstructure is highly crystalline and based on interpenetrating blades. The high anisotropy of the thermal expansion of the crystals leading to microcracking is also thought to contribute to the high toughness.

3.3 Optical Properties

As noted above, it is possible to obtain transparent glass-ceramics. To achieve transparency, the mean size of the crystals must be much lower than the wavelength range of visible light. A variety of systems meet this requirement, some materials being highly transparent with a grain size typically lower than 50 nm and crystal fractions as high as 80–90 vol %. The key to achieving tiny crystals then is to form a very high number of nuclei and to limit crystal growth. In cases such as crystallization of BaF_2 in an aluminosilicate glass [14], crystal growth is limited by the formation of a highly viscous glassy layer at the interface of the crystals. The formation of this layer is related

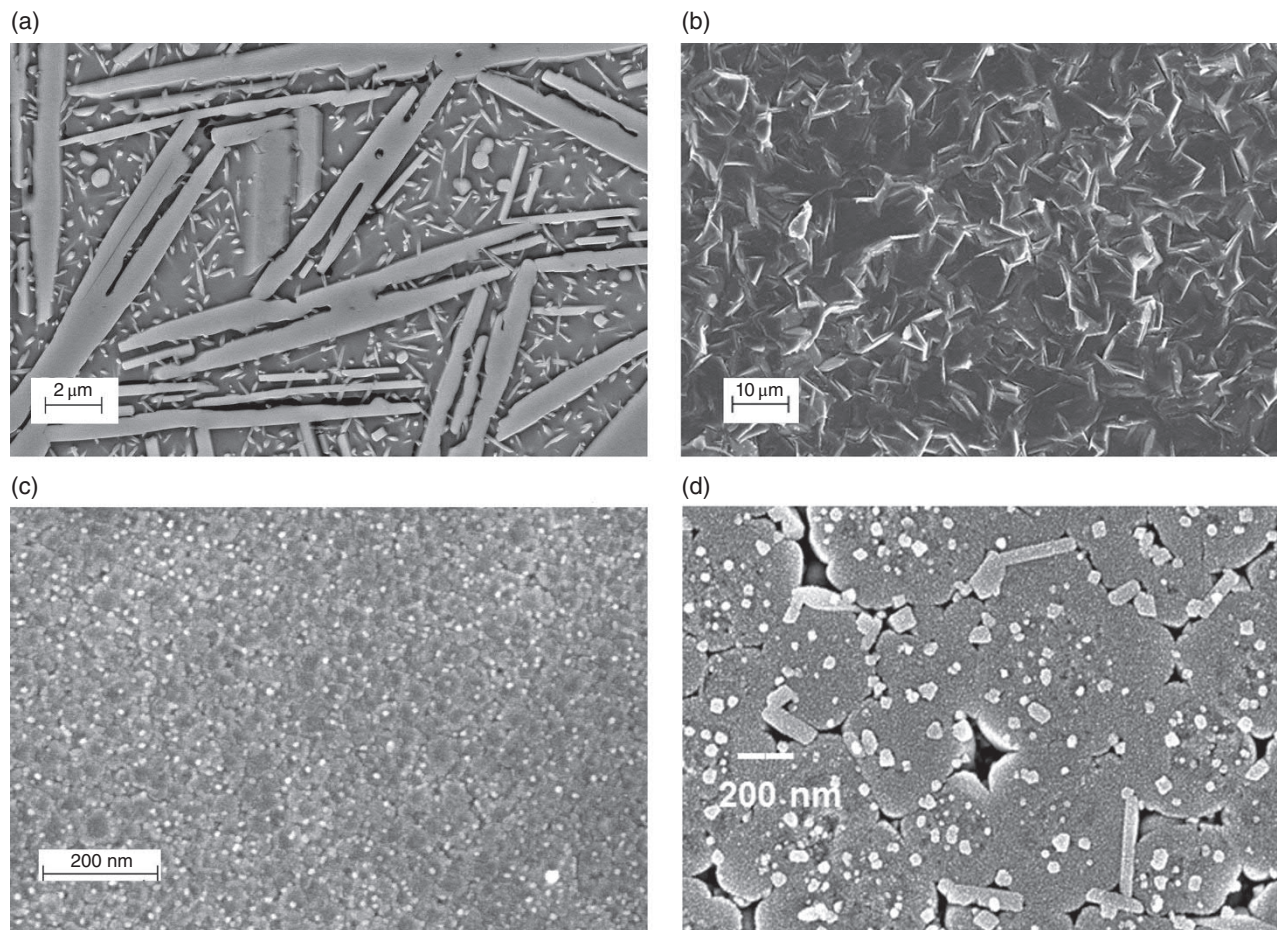


Figure 4 Diversity of microstructures in terms of crystal sizes and shapes obtained in commercial glass-ceramics as observed by scanning electron microscopy (A. Crochet and O. Fraboulet, Corning S.A.S.). (a) and (b) Macor glass-ceramic (main crystalline phase: fluorophlogopite mica) at two different scales. (c) Keralite glass-ceramic (main crystalline phase: β -quartz solid solution). (d) KeraWhite[®] glass-ceramic (main crystalline phase: β -spodumene solid solution). For (a), (c), and (d), the microstructures have been revealed via a chemical attack. For (b), the observation has been made on a fractured sample. For KeraWhite, the pores indicate the former presence of residual glass that has been attacked.

to the depletion of the glass in the more mobile elements, which tend to feed the growing crystals.

To obtain a transparent material, another method would be to match the refractive index of the crystals with that of the residual glass. But, in practice, it is very difficult to satisfy this condition because crystallization is generally incongruent, i.e. the compositions of the crystals and of the residual glass are different. Only a limited number of such materials have been reported. An example is the formation of $\text{Na}_4 + 2x\text{Ca}_4 - x\text{Si}_6\text{O}_{18}$ ($0 \leq x \leq 1$) crystals in a soda-lime glass [15].

Numerous studies have been devoted to optically active materials for applications in the fields of optical communication or solar energy. In this respect, glass-ceramics combine the advantages of a glass phase (i.e. transparency, chemical durability, and ease of fabrication) with those of the crystals into which the active transition-metal or rare-earth ions preferably enter, thanks to the availability of favorable crystallographic sites. Interesting features

such as luminescence or amplification properties have been obtained in several systems, including oxides or oxy-fluorides in which spinels, mullite, and fluoride crystallize, but no product has been commercialized yet [6].

3.4 Rheological and Thermal Properties

As compared with glasses, glass-ceramics offer improved resistance to viscous flow because both the presence of crystals and the preferential partitioning of network-modifier cations into crystalline phase(s) cause viscosity increases that partly oppose the lowering effects of increasing temperatures. The resistance to viscous flow depends on the composition and volume fraction of the residual glass, but materials able to withstand temperatures of 600–900 °C without deformation are common. With alkaline earth aluminosilicates (Table 3), glass-ceramics displaying no deformation up to 1450 °C have been obtained with precursor glasses melted at a

commercially feasible temperature of 1650 °C [6]. In contrast, no rigidification is obtained if the volume crystal fraction is very low. This is, for instance, the case of photochromic glasses, which contain small amounts of silver halides, or of opal glasses containing crystals of sodium fluoride. For this reason, these materials are generally not considered as glass-ceramics.

The bulk thermal expansion of a glass-ceramic is the weighted average of the thermal expansion coefficients of the crystalline and residual glass phases. Because the range of possible values is wider than for glasses, it is possible to tailor the expansion coefficient of a glass-ceramic to specific applications. Glass-ceramics with coefficients higher than $10 \times 10^{-6} \text{ K}^{-1}$ are particularly valuable as sealing materials to metals, for instance, in solid-oxide fuel cells. By contrast, glass-ceramics with almost zero thermal expansion present very high thermal-shock resistance. For example, the Keralite[®] glass-ceramic used as fire-resistant windows withstands thermal shocks of 700 °C (Table 2). On the other hand, β -eucryptite glass-ceramics with negative coefficients as low as $-7 \times 10^{-6} \text{ K}^{-1}$ have even been obtained and proposed as substrates for athermalizing optical fiber reflective grating devices.

3.5 Chemical Durability

Chemical durability is a key property in numerous applications such as consumer products, dental prostheses, and sealing materials. Either through high or low resistance to chemical attack, the specific chemical durability of some crystalline phases and of the residual glass controls the development of numerous products.

For example, the low resistance to hydrofluoric acid of the lithium metasilicate crystals (Li_2SiO_3) allows microstructured materials to be formed by chemical etching (see Section 4.4). On the other hand, the high chemical durability of the zirconolite and pyrochlore phases has led to consider glass-ceramics containing these phases for nuclear waste disposal. The idea is to get the long-lived radionuclides such as actinides preferentially incorporated in the crystals that would be dispersed in a durable residual glass acting as a second barrier of containment.

4 Examples of Glass-Ceramics

4.1 Lithium Aluminosilicate Glass-Ceramics

Products obtained from lithium aluminosilicate glasses represent the main market for glass-ceramics [6, 7]. Their success stems from the combination of several key features, namely, transparency, zero or very low thermal expansion coefficient, and ability to withstand temperatures of at least 700 °C during several thousand hours

without deformation or substantial modification of their properties. They have found a wide range of applications ranging from telescope mirrors to ferrules for optical connectors (produced, for example, by Nippon Electric Glass) or to consumer products such as cooktops, cookware, or fire-resistant windows.

The crystalline phase that yields a transparent low-expansion glass-ceramic is a solid solution with the β -quartz structure. Its general chemical formula is $\text{Li}_{2-2(x+y)}\text{Mg}_x\text{Zn}_y\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ (with $n = 2-10$), where Al^{3+} ions replace Si^{4+} in tetrahedral sites and local electrical neutrality is ensured by the incorporation of small ions such as Li^+ , Mg^{2+} , or Zn^{2+} into the channels of the structure (Figure 5). The thermal expansion coefficient of this phase varies from around -5 to $+5 \times 10^{-6} \text{ K}^{-1}$. It significantly depends on composition such that materials with zero thermal expansion are obtained for $6 < n < 8$ when lithium is the main charge compensator.

In this system, TiO_2 and/or ZrO_2 are very efficient nucleating agents. A high number of nuclei of titanates or ZrO_2 form between 700 and 800 °C and then serve as nucleating sites for the subsequent crystallization of the β -quartz solid solution. The best results are obtained when TiO_2 and ZrO_2 are both present in amounts of 1–2 mol %. In this case, a high number of TiZrO_4 crystals form with a size of a few nm, leaving around them a zone enriched in alumina [9]. For reasons not yet fully elucidated, this zone seems to favor the crystallization of the β -quartz solid solution between 800 and 900 °C. The high number of nucleation sites promotes a high level of crystallization of more than 70% in volume while keeping the size of these crystals below 50 nm, which guarantees transparency.

As noted above, the β -quartz solid solution is metastable. It transforms above around 950 °C to a solid solution of β -spodumene ($\text{LiAlSi}_2\text{O}_6$), with which transparency is lost because of formation of bigger crystals as shown by SEM observations (Figure 4). Some of these glass-ceramics with a β -spodumene solid solution as main crystalline phase retain a thermal expansion coefficient lower than $1.2 \times 10^{-6} \text{ K}^{-1}$ and can resist thermal shocks of at least 600 °C, whence their aforementioned uses as cookware or cooktops (Figures 6 and 7).

4.2 Spinel-Based Glass-Ceramics

Spinel with the general formula $(\text{Mg}, \text{Zn})\text{Al}_2\text{O}_4$ are the main crystalline phases in aluminosilicate glasses containing MgO and ZnO instead of Li_2O [8]. Nucleation is also triggered by TiO_2 and/or ZrO_2 . Transparent glass-ceramics are again obtained because the spinel crystals have a mean crystal size of around 10 nm. As most of the network-modifying cations partition into the crystals, the residual glass is highly siliceous and viscous. As a consequence, these materials can withstand temperatures as

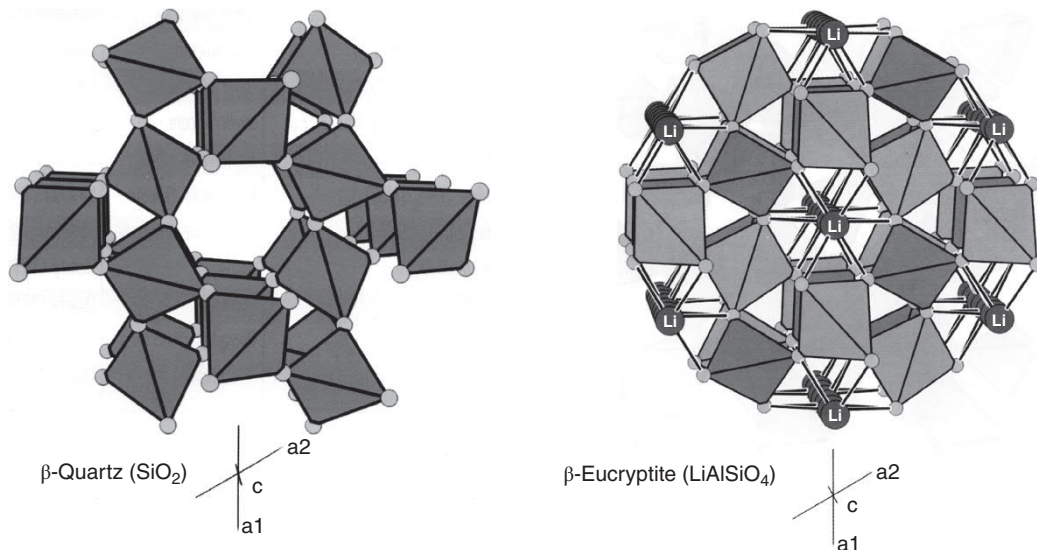


Figure 5 Projection along the c axes of the crystal structures of β -quartz (left) and β -eucryptite (right), the two endmembers of a solid solution that form in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system [6]. SiO_4 tetrahedra appear in dark gray, AlO_4 tetrahedra in light gray. The lithium atoms can be partly replaced by magnesium or zinc atoms.



Figure 6 Examples of Eurokera products made from glass-ceramics containing a β -quartz solid solution as the main crystalline phase. Keralite glass-ceramic (left) is a transparent colorless material sold primarily for fireplace inserts and stove windows. KeraSpectrum[®] glass-ceramic (right) is sold as cooktop material (courtesy Eurokera S.N.C.).

high as 1000°C without sagging and losing their transparency. With values in the 3 to $4 \times 10^{-6} \text{ K}^{-1}$ range, their thermal expansion is close to that of silicon. Consequently, they have been envisioned as substrates for flat screens or photovoltaic devices.

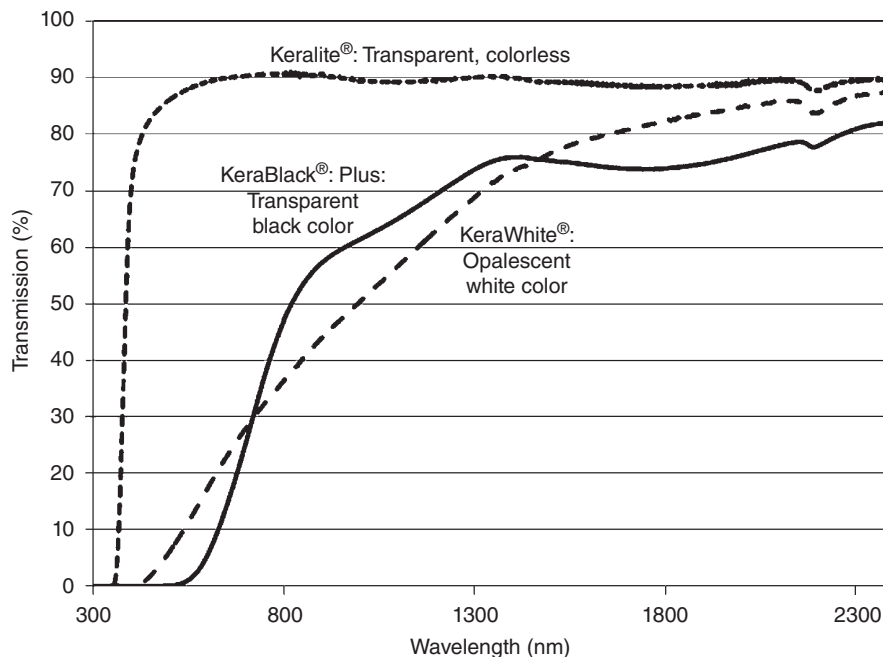
4.3 Magnesium Aluminosilicate Glass-Ceramics

Cordierite glass-ceramics that are used to make radomes belong to this system. Cordierite has been chosen because it can yield materials with relatively low expansion, high mechanical strength, high elastic modulus, and

transparency to microwave signals used for guidance. In this case bulk nucleation is obtained with TiO_2 [6].

It is also possible to obtain cordierite glass-ceramics via surface nucleation [11]. The process allows strip conductors made of copper, silver, or gold to be encapsulated through cofiring below 1000°C . This method has thus been used to make substrates for electronic packaging as an alternative to Al_2O_3 for which cofiring is performed at 1500°C . In addition to such sintering properties, these materials present the advantage of a low dielectric constant (4–6 as compared to 9 with alumina).

Figure 7 Relative transparency of glass-ceramics produced by Eurokera as indicated by their transmission as a function of wavelength.



4.4 Lithium Silicate Glass-Ceramics

It was with lithium silicates that S. D. Stookey serendipitously obtained the first glass-ceramic nucleated in volume, silver colloids having acted as the nucleating particles. With P_2O_5 as nucleant, one obtains glass-ceramics with very high mechanical strength where the main crystalline phase is $Li_2Si_2O_5$ [5, 6]. These materials are of great interest for dental restoration because they retain some transparency (Chapter 8.5).

Another interesting property of lithium silicates is that their nucleation can be controlled by irradiation (Figure 8) when small amounts of a silver salt and cerium oxide are introduced in the base glass composition. Under irradiation in the 290–330 nm wavelength range, a redox reaction between silver and cerium ions takes place in that silver colloids form while cerium is oxidized. These colloids then serve as nuclei for subsequent Li-silicate crystallization. A mask can limit the irradiated zone over which lithium metasilicate (Li_2SiO_3 , a metastable phase) subsequently forms as fine dendrites. Because lithium metasilicate is highly etchable, it is possible to perform a preferential chemical attack of the crystallized areas and to obtain in this manner a microstructured material. This material is glassy but a glass-ceramic can also be made to increase mechanical strength: for this purpose, an additional irradiation is performed and followed by a thermal treatment in the 800–900 °C range in order to precipitate the lithium disilicate phase ($Li_2Si_2O_5$), which is chemically durable.

These materials are produced by Corning under the names of machinable glass Fotoform and machinable

glass-ceramic Fotoceram, and by Schott under the name of machinable glass Foturan®. With microstructures having a size of 25 μm and a roughness of about 1 μm , these materials are used to make components with a high dimensional precision in the fields of micromechanics, microoptics, and fluidics, for example, where they have the additional advantage of being connectable without any intermediate layer by thermal diffusion bonding. The company Mikrogas has proposed micro-reaction systems for the manufacture of chemical and/or pharmaceutical products made with the machinable glass Foturan.

4.5 Fluorinated Phase Glass-Ceramics

Addition of a few percent of fluorine to silicate glasses allows a wide range of crystals containing this element, such as micas and amphiboles, to be formed. The sequence of crystallization is generally complex. The nucleation mechanism most often begins with phase separation. Crystals such as CaF_2 or MgF_2 then precipitate before transforming into other phases, which give rise to the final microstructure [5, 6].

Among the interesting microstructures obtained with these materials, the interlocking of acicular crystals such as canasite or amphiboles yields outstanding mechanical strength. Another example is the “house of cards” microstructure that ensures machinability in glass-ceramics containing micas as the main crystalline phases and allows materials with a variety of complex shapes to be produced with conventional metal-working tools (Figure 9).

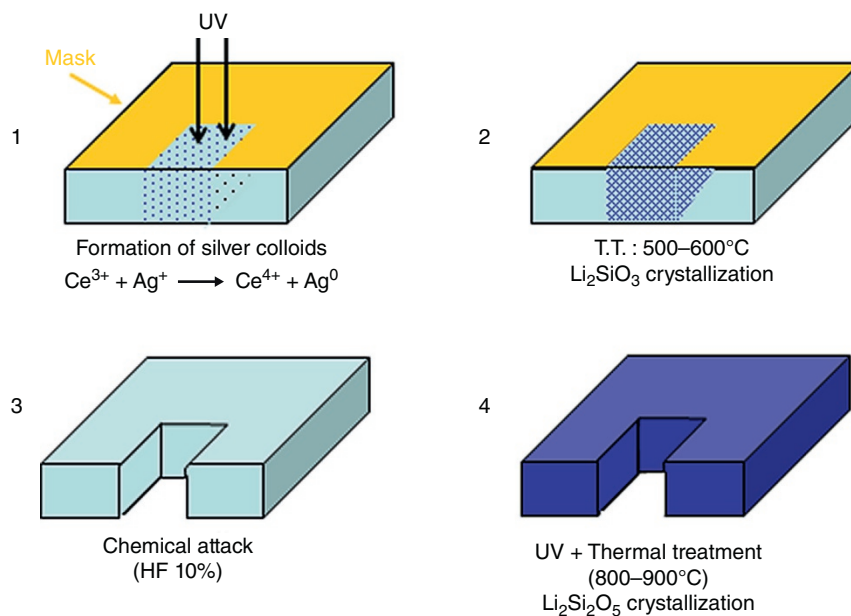


Figure 8 Sketch of the machinable glass Fotoform and machinable glass-ceramic Fotoceram fabrication process. The microstructured glass obtained at step 3 is called machinable glass Fotoform, the microstructured glass-ceramic obtained at step 4 is machinable glass-ceramic Fotoceram.



Figure 9 Examples of pieces produced from machinable Macor glass-ceramic (Corning S.A.S.). Having excellent physical properties, high dielectric strength, and electrical resistivity, the MACOR® glass-ceramic is nonporous, non-shrinking, and withstand high temperatures. In addition, it can be given any complex shapes with conventional metal-working tools.

The trick is that mica platelets are mutually connected and oriented in all directions, thereby isolating pockets of residual glass that represent about 50 s% of the volume of the material (Figure 4). The crystals tend to block and deviate the cracks so that damage is limited to the glass domains. The connection of the crystals gives other advantages to these materials: lack of creep and deformation up to 800 °C, high resistivity, high dielectric strength, and very low helium permeability. Several companies manufacture such materials under the names of machinable Macor®, Vitronit®, and Macerite® glass-ceramics. These materials are used as technical pieces in various domains such as the electronic, semiconductor, or vacuum industries.

4.6 Glass-Ceramics Based on Phosphate Glasses

Phosphate glass-ceramics are mainly used in medical applications and as ion-conductive materials.

In the medical field, two types of applications exist for dental prostheses and bone implants (Chapters 8.4 and 8.5). For dental prostheses, the key properties are mechanical strength, chemical durability, and translucency. A wide range of materials have been commercialized. Among them, glass-ceramics of the $\text{P}_2\text{O}_5\text{--SiO}_2\text{--Li}_2\text{O--ZrO}_2$ system are produced by Ivoclar Vivadent. The content of ZrO_2 exceeds 15 wt %, which is key for mechanical strength.

Requirements for the implant materials are different, in that biocompatibility and eventually bioactivity are necessary. Apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{O}, \text{F})_2$, is generally one of the main crystalline phases that form in the phosphate or silicophosphate glass-ceramics used for these applications.

Under the name LICGC™ (lithium-ion conducting glass-ceramic), Ohara sells a material that can be used as solid electrolyte in advanced batteries. The main crystalline phase is a solid solution of Nasicon with the formula $\text{Li}_{1+x+y}\text{Al}_x(\text{Ti, Ge})_{2-x-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ [16]. The high ionic conductivity stems from the structure of the Nasicon phase where the alkali cations occupy sites in interconnected channels formed by corner-sharing tetrahedra and octahedra.

5 Perspectives

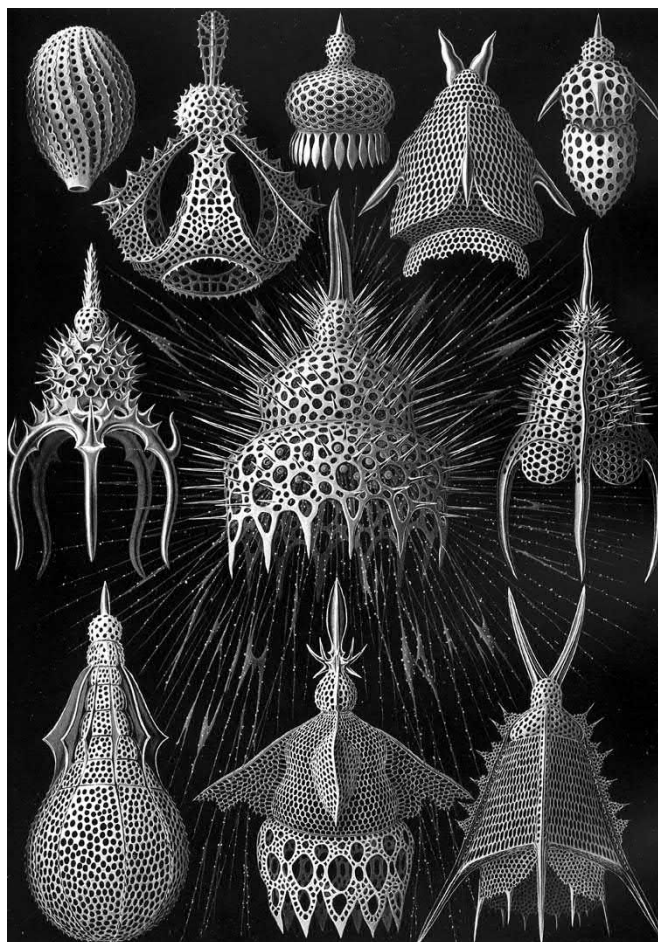
Although the history of glass-ceramics is rich in commercial successes, these materials have been developed in the past in a quite empirical way. Nucleation and growth mechanisms were not easy to study because of the complexity of the glass compositions and of the small size of the first nuclei. The important advances recently made in understanding glass structure and in developing analytical methods have considerably increased our knowledge of the nucleation and growth mechanisms in glasses. Such research could be a key enabler for novel materials with outstanding properties. Numerous potential applications can be envisioned. In the future, glass-ceramics will likely serve as key components of products in such demanding fields such as health, energy (solar cell, sealing of solid-oxide fuel cells), and environment (recycling of waste products, including nuclear waste), where materials combining several key properties are required. Research is already very active in these areas.

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Section VIII. Organically Related Glasses

Figure 1 The astonishing shaping versatility of biogenic amorphous silica: the shells of some radiolarians drawn by Ernst Haeckel in his famous three-volume book *Die Radiolarien* (1862–1888).



One of the best-kept secrets regarding amorphous silicates is that man is by any standard a negligible maker in comparison with nature: the yearly world production of 120 million tons of glass represents a few per mille of the amount of the amorphous silica synthesized either on land by plants in concretions named *phytoliths* or in the sea by animals like sponges, the *radiolarians* of the zooplankton (Figure 1), and especially by the *diatom* photosynthetic algae. The processes involved appeared relatively late in the evolution history and gave competitive advantages to mechanically strong and optically clear amorphous silica over polycrystalline carbonates whose amorphous forms are highly unstable. As described by J. Livage and P.J. Lopez, this silica synthesis plays a fundamental role in the global cycles not only of silicon but also of carbon and nitrogen; it is taking place under biological control via silanol polycondensation reactions at room temperature, and it has fostered the *biomimetic* design of new materials inspired, for example, by the nanostructured *frustules* of diatoms, with which photosynthetic activity is optimized, or by the fibers of outstanding optical properties of the sponge *spicules* (Chapter 8.1).

In sol–gel processes, the starting materials are liquid organometallic precursors that are mixed at room temperature and transformed into a gel before being dried and sintered in the bulk or as porous pieces, fibers, or thin films depending on the intended application. As explained by R. Almeida and C. Gonçalves, by-passing any treatment at temperatures higher than the glass transition range allows synthesis of markedly metastable glasses that would otherwise unmix or be impossible to deposit on the surface of other materials; practical problems are large shrinkage upon processing or difficulties in eliminating hydroxyl species, whereas the very high cost of the starting products restricts the processes to high value-added products whose market is nonetheless growing rapidly (Chapter 8.2). Special but important cases of sol–gel products are the silica aerogels presented by W. Malfait et al. whose densities can be as low as 0.2 g/cm^3 and thermal conductivities are negligibly small because their nanopores have a size smaller than the mean free path of air molecules; as a result, aerogels are superinsulating materials, whereas their very high specific surface areas of up to $1000 \text{ m}^2/\text{g}$ make them valuable for other uses such as catalyst supports (Chapter 8.3).

An even more rapidly growing field is that of bioglasses. The originality of these new materials is not to be used as permanent prostheses, but rather to stimulate the regeneration of the bone or other tissues by surface reactions that promote natural cell attachment and proliferation. Like for water glass, the key feature of bioglasses discussed by D. Brauer and J. Jones is the intrinsic reactivity of depolymerized calcium- and phosphorus-bearing glasses (produced by melting or sol–gel processes) that

is ensured by their high concentrations of nonbridging oxygens and network modifiers, so these glasses serve as starting materials for spontaneous tissue repair (Chapter 8.4). For dental restoration with onlays, veneers, or bridges, permanent stability is in contrast required. Common glass ceramics (Chapter 7.11) are thus used. As reported by W. Höland and M. Schweiger, the important features engineered with leucite or lithium disilicate glass ceramics are not only high mechanical properties but also ready machinability, resistance to thermal shock, and the possibility to simulate the aspect and hue of teeth with materials that must be clearly distinguishable in radiography (Chapter 8.5).

The rest of the section is devoted to organic glass-forming liquids. As a sequel of the general picture of relaxation given in Chapter 3.7, the contribution by T. Blochowicz, E.A. Rössler, and M. Vogel first describes the additional mechanisms present when the existence of well-defined molecular entities makes rotational degrees of freedom enter the scene; these entities can freeze in at temperatures lower than that of the remaining of the substance and give rise to secondary relaxation processes persisting in the glassy state (Chapter 8.6).

The two following chapters are devoted to organic polymers, which have become the most important glasses in terms of quantities produced. From a mere 2 million tons in 1950, this production reached 335 million tons in 2016 (about 50% in Asia and 20% in both Europe and North America, cf. www.plasticseurope.org) and will keep growing in spite of environmental concerns in particular raised by insufficient recycling in many countries. Compared with silicate glasses, the production is about greater by a factor 3 in terms of mass but of nearly 10 in terms of volume as a result of the large density difference between these two kinds of materials. Although their diversity of uses is not as great, polymers have become indispensable and displaced silicate glasses for many food and beverage containers as well as for high-tech optical applications such as eyeglasses and camera lenses in smartphones (Chapter 6.1). But both kinds of materials complement each other remarkably well in composite materials made up of epoxy resins and reinforcement glass fibers (Chapter 1.6).

In dealing with the physics of organic polymers, J.-P. Cohen-Addad mainly focuses on (i) their very long molecular chains made up of concatenated identical monomers of relatively low molecular mass, within which bond rotation freely takes place in the liquid state; (ii) their viscoelasticity produced by the elastic deformation of the chains and their random motion, which causes viscous flow; (iii) and how the polymer structure can be tailored through partial crystallization or chain cross-linking and may eventually age over the years (Chapter 8.7). Differences in the building, cross-linking, and degree of

polymerization of the various monomers are at the origin of the diversity of polymers and, in particular, of the distinction made between *thermoplastics* (e.g. polystyrene, polypropylene, polyamides, PVC) and *thermosets* (e.g. polyurethane, epoxy, and acrylic resins) depending on whether their curing-induced hardening is reversible or not. Polymerization mechanisms are of two kinds, chain and step growth, as reviewed by O. Weichold who explains how and under what conditions they are controlled in industrial synthesis, why the glass transition temperature is the fundamental theoretical and practical parameter, how it is related to the polymer structure, and how it can be lowered by plasticization (Chapter 8.8).

As exemplified by the aforementioned reinforcement of epoxy resins with glass fibers, composites represent

combinations of different materials at a macroscopic scale such that each keeps its individuality and properties. In the new *hybrid* organic–inorganic polymers described by K.H. Haas and G. Schottner, the combination is in contrast effected at a microscopic level between the structural components of each phase to obtain a homogeneous material combining the advantages of both; owing to a priori structural incompatibilities illustrated by considerable differences in the glass transition temperatures of their components, they must be synthesized via sol–gel processes: the bulk pieces, coatings, powders, and fibers can be produced over wide ranges of fractions of organic and inorganic components with the appropriate starting organometallic precursors (Chapter 8.9).

8.1

Biogenic Silica Glasses

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1 Introduction

Two impressive figures neatly summarize the importance of amorphous silica synthesis by living beings in both aqueous and land environments. For the micro-phytoplankton of the oceans, the yearly silica production is estimated to be 240 Tmol of Si [1] or 15 billion tons – i.e. about 150 times the world glass production – most of which is assigned to a single class of the photosynthetic unicellular algae, the *diatoms*. As for *phytoliths* (from *phutos*, plant, and *lithos*, stone), the silica inclusions present in terrestrial plants ranging from moss, fern, grass, and rice to a variety of trees represent 80 Tmol of Si [2] or 5 billion tons of SiO₂ per year. Given that diatoms account for 35–75% of the marine net primary production [1] and for about 20% of photosynthetic activity on Earth [3], then it becomes obvious that biogenic silica is playing a major role in the global ecosystem. In other words, life has managed to integrate silicon in the metabolism of a great diversity of aquatic and terrestrial organisms, drawing Si from the solute species dissolved in their environments [4].

It has been obvious for centuries that the silica cell walls termed *frustules* (from *frustulum*, small piece in Latin) or *thecae* (sheaths, in Latin) bring protection to diatoms. But the regular and aesthetic pattern of the holes present on frustules was only recently shown to present optical properties [5]. Knowledge about the fundamental aspects of this biogenic production is also relatively recent since the first molecular data were obtained in the early 2000s whereas the biochemical mechanisms of frustule synthesis are only beginning to be understood [6, 7].

Although sponges have much less biological importance than diatoms, some species of these extremely simple animals distinguish themselves by their silica *spicules* whose optical properties rival those of the best commercial fibers [8]. These two examples thus nicely illustrate the interest currently paid to *biomimeticism*, the concept by which attempts are made at imitating the sophisticated nanostructures found in nature to produce new materials with original properties.

Phytoliths, which have also been known for a long time, are lurking in the background of the Si cycle since this element is necessarily transported in plants in the form of water-soluble silicic acid, Si(OH)₄, the starting point for SiO₂ polymerization. The fundamental interest they have recently raised is not related to biomimeticism, but rather to the role of silicon in the nutrition, physiology, and defense of plants [9]. Beneficial effects brought by silicon dioxide, for instance, include resistance against drought, salinity, heavy metal pollution, and other abiotic stresses, as well as against attacks by insect herbivores or parasitic animals and plants. In rice, Si even appears to be actively involved in the plant metabolism.

Biogenic silica thus presents a dual interest either through its biological role or as a material itself. These two features will be addressed in this chapter. A few significant historical aspects of the discovery of biogenic silica will be described first. Next, the production and most outstanding properties and uses of the silica produced by sponges, diatoms, and plants will be reviewed. The stage will then be set to deal with the physical properties of biogenic silica, its condensation from silicic acid, and the mechanisms involved in its synthesis by aquatic organisms and plants from Si dissolved in natural waters and soils at concentrations as small as 10^{−6} mol/l. In the last part, the issue of biomimeticism for green chemistry and nanotechnologies will be addressed along with the

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connections between the cycles of silicon, carbon, and nitrogen in the global ecosystem. Finally, fundamental aspects of evolution will be briefly mentioned. Of particular interest are the appearance of biogenic silica and also the advantages that this phase conferred along the evolutionary tree over calcium carbonates, which are actually much easier to synthesize. Although an amorphous calcium carbonate forms as an intermediate reaction step in these syntheses, a marked difference with biogenic silica is the intrinsic instability of this amorphous phase [10, 11].

2 A Slowly Awakening Scientific Interest

In the instance of the *Tabellaria* genus, diatoms were first described in 1703 by an anonymous observer as an *animalcule* [12] in the early days of microscope studies (Chapter 10.10). After diatoms were recognized to be algae in 1844, it was the extreme morphological variety of their frustules that specially drew the attention of naturalists (Figure 1). In the fourth edition of his epoch-making *Origin of Species*, Charles Darwin (1809–1882)

pointed out in 1866 that “few objects are more beautiful than the minute siliceous cases of the diatomaceae” before wondering: “were they only created to be admired under the microscope? The beauty in this latter case, and in many others, is apparently wholly due to symmetry and growth” [13]. At the same period (Figure VIII), the 50–300 mm silica tests of the unicellular *radiolarians* remarkably well pictured by Ernst Haeckel (1834–1919) in his *Die Radiolarien* [14] made so strong an impression on the general public that these members of the zooplankton then served as a model for the entrance pavilion to the famous 1900 Paris World Fair (Figure 2)!

Was Darwin aware in 1866 that the frustules of diatoms accumulating as lacustrine sediments had long been mined as a siliceous source for a variety of uses in the form of *Kieselguhr* (German *Kiesel*, gravel, and *guhr*, wet matter issued from rock)? By a strange coincidence, *Kieselguhr* found a high-tech application when Alfred Nobel (1833–1896) discovered the following year that it was the ideally inert, absorbing porous material needed to stabilize the violently explosive nitroglycerin, which had killed his young brother in 1864. Diatom frustules were thus a key component of his hugely successful commercial product named *dynamite*, to which Nobel Prize winners have owed a great deal since 1901.

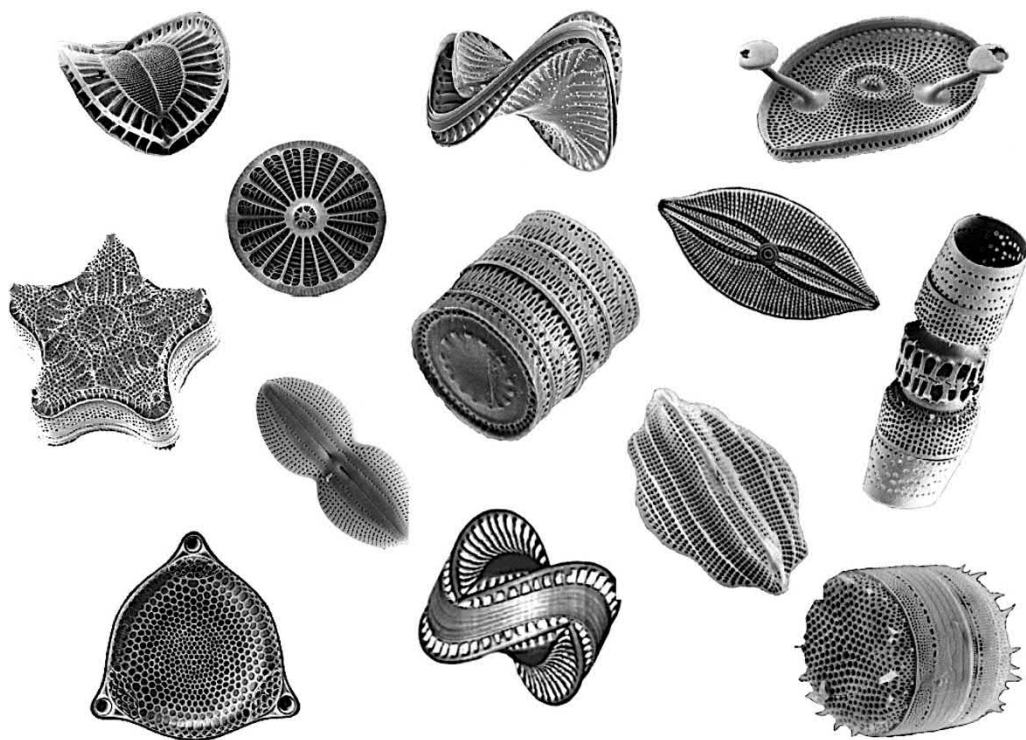


Figure 1 The extreme morphological variety of diatom frustules and the specificity of their hole patterns shown by scanning-electron micrographs of a few species among the 100 000, grouped into 200 genera, which are distinguished by their morphology with sizes ranging from 2 to 200 μm .

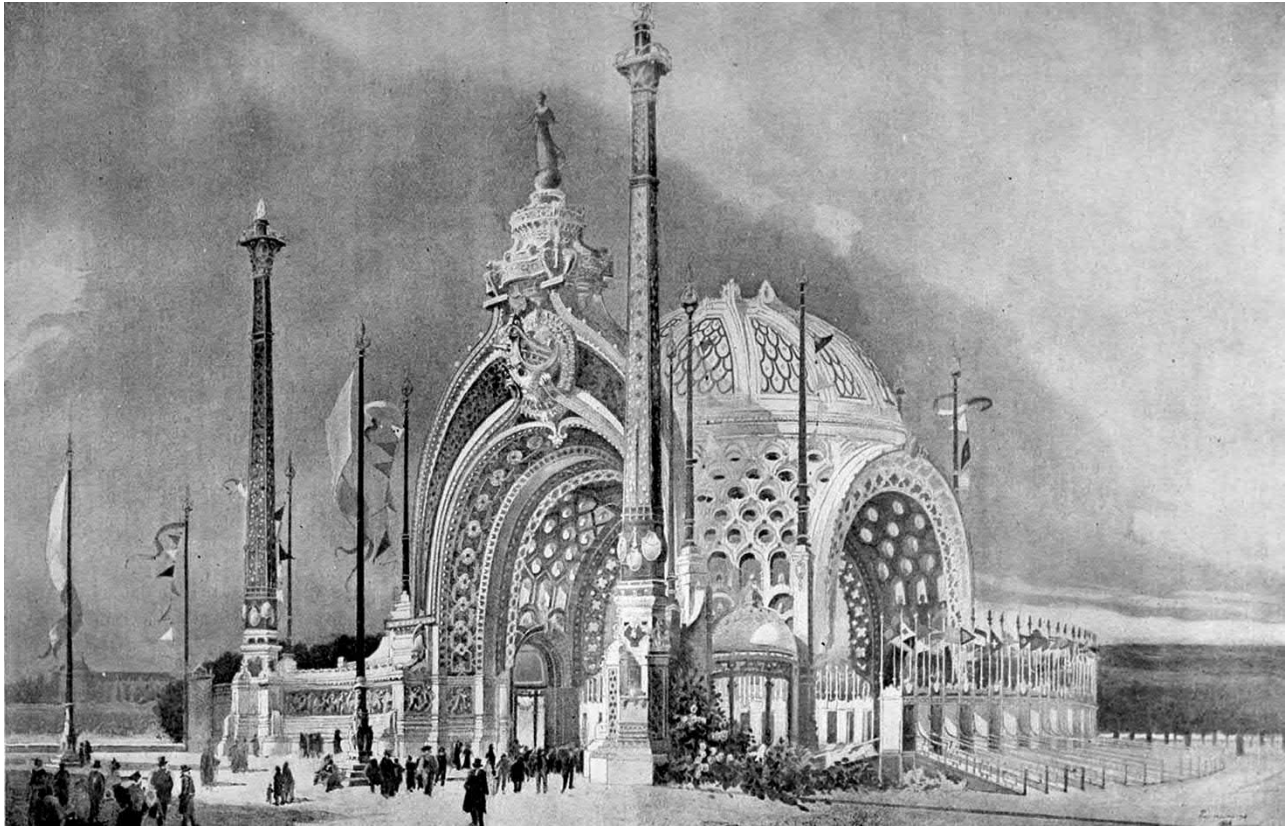


Figure 2 Haeckel's drawings of radiolarites as a source of architectural inspiration: the entrance pavilion to the 1900 Paris World Fair popularized by a postal card; René Binet, architect (1866–1911).

In Asia, it was the interlocked silica skeleton built by the deep-sea *Euplectella aspergillum* sponge that got some notoriety. In this *glass house* (Figure 3), a male and a female of a small species of crustaceans often live symbiotically with their host. The sponge provides for the food and safety of the couple, which in return keeps cleaning the basket without being able to leave it. Only their offspring are small enough to go out in order to find their own host sponges. One can thus understand why these *Venus flower baskets* were offered as bridal gifts in ancient Japan. However, the remarkable mechanical properties of the meter-long silica *spicules* grown by other sponges [15] have long escaped attention. Likewise, the special optical properties of these silica fibers have been recognized only recently [8].

As for phytoliths, they were assigned antipyretic, antispasmodic, antiparalytic, and (of course) aphrodisiac virtues in Asia in the form of the bluish or yellowish *tabashir* concretions formed in the knots of some species of bamboo. From time immemorial, in contrast, reapers did not know that it was the presence of such tiny, hard inclusions in the soft tissue of grass that required their scythes to be sharpened so frequently. It was the Genevan naturalist

Théodore de Saussure (1767–1845) who noticed the high concentration of silica in the ashes of a wide variety of plants, especially in grass and other ubiquitous Gramineae [16]. Phytoliths were discovered a few decades later by Gustav Adolf Struve (1812–1889) [17] and began to be studied in a systematic way soon after by Christian Gottfried Ehrenberg (1795–1876) [18]. It has then become apparent that they improve not only some mechanical resistance to predators but, as already noticed, also to a variety of stresses in natural environments [9]. With a size typically ranging from 10 to 100 μm , phytoliths also exhibit a wide diversity of shapes, which are species specific (Figure 4). Not surprisingly, phytoliths are much less prone to alteration than their parent plants, even in tropical climates, and may withstand fire and digestion by animals. Thanks to their taxonomically distinctive nature, phytoliths are thus now extensively used in archeology or ecology as tracers of past events. When some carbon is included in phytoliths, an additional advantage is the possibility to perform ^{14}C radioactive dating of their context. To name just a few, topics investigated, thanks to phytoliths, include grass grazing by dinosaurs 70 million years (My) ago, natural shifts in vegetation and climate,

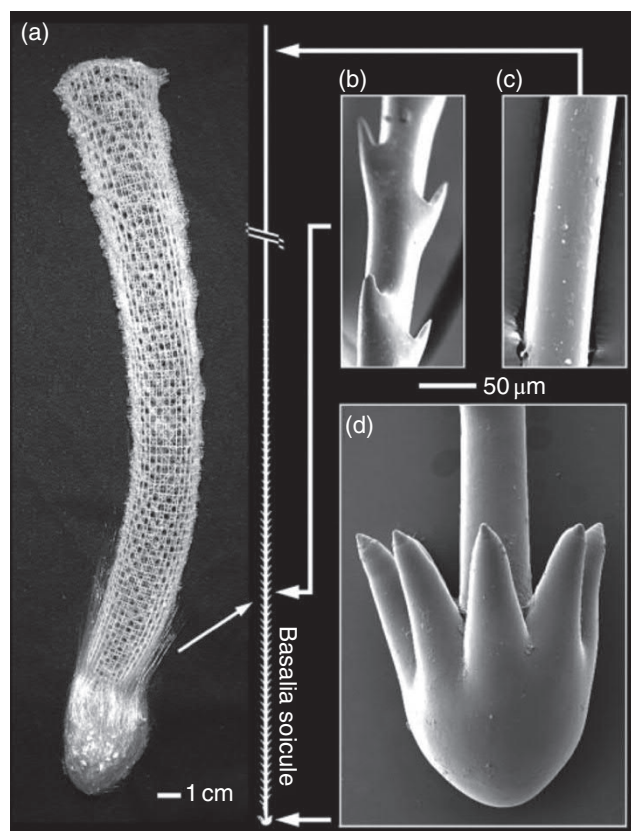


Figure 3 The Venus flower basket of the *Euplectella aspergillum* sponge [8]. Size ranging typically from 10 to 30 cm, sometimes up to 1.3 m. (a) Fused silica spicules built from a basal crown; (b–d) scanning electron micrographs of the spined proximal region, of the smooth distal region of a basalia spicule and of its apical process, respectively. Source: Reproduced with permission © (2004) National Academy of Sciences, USA.

processes and diffusion of plant domestication, or the agricultural practices or diet of populations in most diverse archeological settings [20].

A somewhat related question deals with the biological effects of silica absorbed with the food on human health. There is a quasi-continuum of Si species between amorphous SiO_2 and Si(OH)_4 through di- ($\text{H}_2\text{Si}_2\text{O}_5$), tri- ($\text{H}_2\text{Si}_3\text{O}_7$), pyro- ($\text{H}_6\text{Si}_2\text{O}_7$) silicic acids and higher oligomers. Insufficient levels in Si, which is the third most abundant trace element in the human body, have been related to conditions such as osteoporosis, skin aging, atherosclerosis, Alzheimer's disease, and other degenerative processes [21]. Silicon transport has also been demonstrated to take place in humans, opening the way to new investigations of the physiological role of silicon in vertebrates [22, 23]. A mean daily intake of 12 mg of Si per kg of body weight has been recommended. Cereals, fruits, and vegetables are the most abundant Si sources in

foodstuff. Consistent with the presence of phytoliths in animal dung, however, the bioavailability of amorphous silica and polymeric silicic acids is poor. Phytoliths thus have little prospect of becoming food supplements; zeolites seem to be better alternatives [21].

3 Biogenic Silica

3.1 Sponge Spicules

Sponges are among the earliest and simplest animals. More than 550 million years (My) ago, they appeared during the Cambrian as multicellular aquatic beings devoid of any tissue or organ [24]. Thanks to flagellated cells, they feed on organic matter and bacteria brought by the water that circulates through the 3-D open structure of their pores and canals. If sponges are of course well known for their softness, many species build internal skeletons made up of calcium carbonate or silica. Representing up to 75% of the sponge biomass, the silica skeletons display a high diversity of shapes and sizes. They support the sponges, help during the development along functional body plans, enhance their reproduction success, improve their mechanical strength to endure hydrodynamic forces, and may act as deterrents for predators [25, 26].

The so-called *glass sponges* (*Demospongiae* and *Hexactinellida*) are found worldwide, mostly in deep waters where they grow attached to hard or soft substrates. Their twisted basal stalk is anchored in sediment whereas the upper parts etch a circle by bending and swaying in deep-sea currents. As built around a proteinic axis by cells called *scleroblasts*, their spicules are durable, some of them are flexible, and almost unbreakable. Their sophisticated ultrastructure can involve a 3-D collagenous network that is not only present in the central channel but also extends radially in between the silica layers (Figure 5) [25, 27]. These two components thus give rise to an anisotropic composite material in which the lamellar layers at the spicule periphery connected by bridging organic ligands are effective to stop crack propagation upon bending or twisting. In *Porifera hexactinellida*, the average breaking stress of 593 ± 165 MPa is thus almost four times higher than for pure SiO_2 glass (155 ± 28 MPa) [15]. But the Young's modulus of 36.5 GPa of the former is half that of the latter probably as a result of the weakening effect of the water present in the structure [15]. In subsequent studies, still higher fracture stresses have been observed upon tensile and bending tests, for example, with values of 1895 ± 325 and 3727 ± 661 MPa, respectively, for the 40 μm in diameter spicules of the aforementioned *E. aspergillum* [28].

Figure 4 The diversity of shapes of phytoliths found in 10 000–5 000-year old mountain soils in Brazil: (a) polylobate, (b) bilobate, (c) cross, (d) rondel, (e) trapezoiform, (f–i) acicular [19].

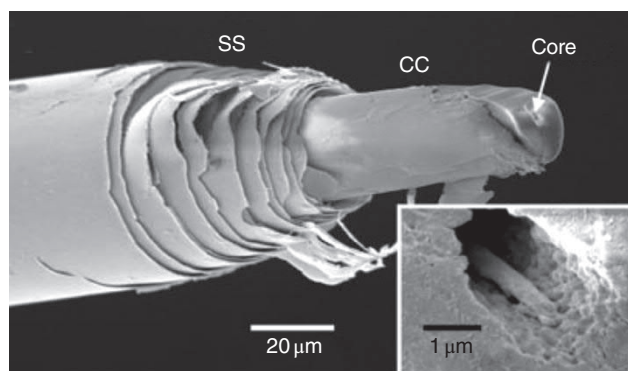
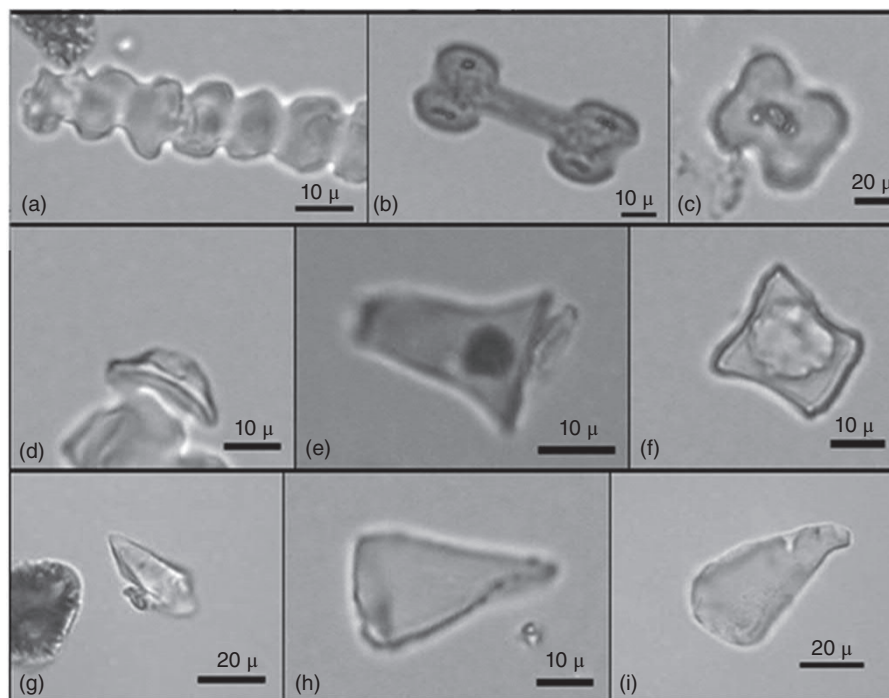


Figure 5 The concentric structure of a basalia spicule of the *Euplectella aspergillum* sponge as revealed by a scanning electron micrograph after etching with fluorhydric acid [8]. CC, smooth central cylinder; SS, striated shell region. Inset: organic filament seen by high resolution in the etched core. Source: Reproduced with permission © (2004) National Academy of Sciences, U.S.A.

The spicules of this species in addition exhibit remarkable optical properties. Their distinctive layered design translates into variations of composition and properties within the glass/organic composite as exemplified by the refractivity difference between: (i) a 1–2 μm in diameter Na-doped core with a high index of 1.45–1.48, which may thus be higher than that of silica (1.458); (ii) a 15–25 μm cladding with an index that can be as low as 1.425; and (iii) an outer portion where the index increases progressively from 1.433 to 1.438 [8]. In addition to trap and transport light, spicules can function as single-mode,

few-mode, or multi-mode fibers (Chapter 6.4). These spicules are strong, resist to stress, and form their own supporting elements. Their formation at ambient temperature makes an increase of the refractive index of the fiber possible through the incorporation of impurities such as Na without promoting crystallization. Likewise, residual stresses cannot build up to cause birefringence as often observed in commercial fibers. Finally, the presence of terminal lens-like extensions and barb-like spines along the spicule shaft improve light collection [8]. Spicules may thus be considered as waveguides, which could compete with some of the best commercial optical fibers, to transmit optical, electrical, or even chemical signals, and thus carry information to the cells about their environment. However, the biological role or implications of such light transducing capability are still unknown and very unlikely to occur in most of the natural deep-sea environments within which scleractinian sponges can be found.

3.2 Diatom Frustules

Even if their origin, proposed in the early Mesozoic (250 My ago), from marine or freshwater environments is still a matter of debate [29, 30], diatoms deposits from fresh water dated to the Lower Jurassic (175 My) have been reported. Although their biomass is most significant in the oceans, diatoms are really ubiquitous as they also live in estuaries, rivers, lakes, ponds, puddles, and even in soil or on wetted plants and rocks.

Representing the wall of their cell, their silico-organic frustules are made up of two parts, of slightly different sizes, connected by *girdle bands*. In fact, when diatoms divide during their cell cycle, the new valves (and also girdle bands) are reconstituted within few hours within a specialized cellular compartment, the silica deposition vesicles (SDV). Regardless of their shape, frustules are highly porous to allow for metabolic exchanges with the outside aqueous medium, transparent to light, and also rigid in order to protect the cell against predators (mainly grazing *copepods*, i.e. small herbivorous crustaceans). Indeed, the frustules of living diatoms exhibit outstanding mechanical properties. For example, the oval-shaped frustules of *Fragilariopsis kerguelensis*, the most abundant species in Antarctic seas, can, for instance, sustain estimated maximum stresses of 540 MPa whereas the ultimate tensile and compressive stresses of the valve and girdle are 560 and 680 N/mm² and 155 and 330 N/m², respectively [31]. Although their Young's modulus of 22.4 GPa is lower than that of pure silica glass (73 GPa), it is close to those of cortical bones (20 GPa) and dental composites (6–25 GPa) [31–33]. This feature is likely one of the reasons why diatoms have been biologically so successful compared with other algae.

Some silica frustules exhibit a hierarchical distribution of pore sizes. The genus *Coscinodiscus*, for instance, exhibit three layers of pores containing small (≈ 10 nm), medium (≈ 100 nm), and large pores ($\approx 1 \mu\text{m}$) (Figure 6). These pores are not randomly distributed but rather ordered in a periodic 2-D network with a basal spacing of few tenths of microns (Figure 7). Diatom frustules exhibit iridescence and are often referred to as “sea opals” with the important feature that they focus visible light while reflecting UV rays [5, 34–36].

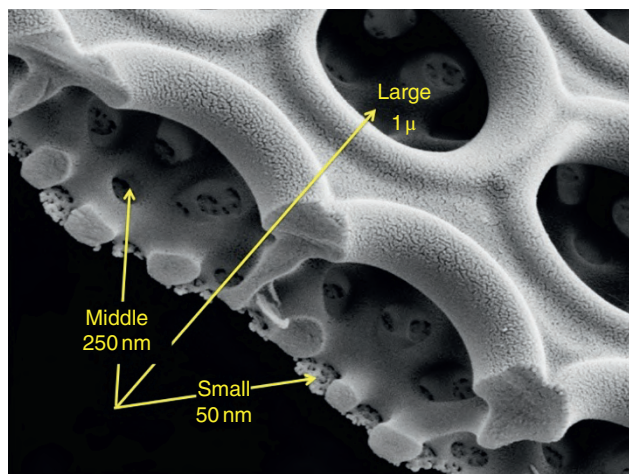


Figure 6 Scanning electron micrograph revealing the hierarchical distribution of pores on the frustule of *Coscinodiscus* sp.

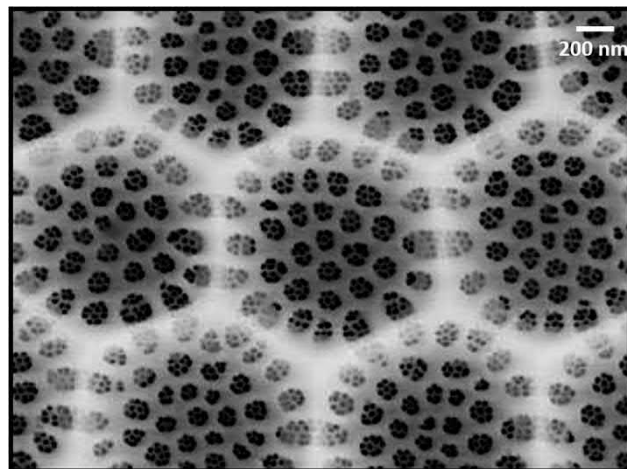


Figure 7 The 2-D periodic network of *Coscinodiscus* sp.

After dying, diatoms sink and escape dissolution in part, thanks to the organic materials, and can then accumulate as beds interspersed with other. Once deposited, the frustules slowly compact and transform into *diatomite*. In the process [37], the 3-D network structure of amorphous silica develops through a decreasing fraction of Si atoms bearing silanol groups (Si-OH) and a concomitant increase of the fraction of Q^4 species (Chapter 2.4). Already known in Antiquity, diatomite is a rather pure, inexpensive, and soft raw material widely exploited in open-pit mines (Figure 8). It mainly consists of wet amorphous silica, but also contains up to 3% of quartz. The extracted product is gently crushed, dried, and milled and, depending on purity and use, it can be calcined between 850 and 1000 °C in large rotary kilns to remove moisture and organic products. Upon calcination, up to 40% of the amorphous silica can transform into cristobalite, the high-temperature SiO₂ polymorph. The proportion can even reach 70% when soda ashes (sodium carbonate) are used as a flux to promote sintering during calcination. After calcination, the generally whiter product is crushed and sifted in different categories depending on the grades to be commercialized.

The main producers of diatomite in 2016 were the United States (850 kton), Czechia (450), China (420), followed by Argentina (200), Peru (150), Japan (100), Mexico (90), France (75), and Russia (70). The rest of the world accounts for 220 kton. Because of its chemical inertness, large specific surface area, and tiny pores of the frustules, diatomite is used in thousands of common products. It is best known as an excellent material for liquid filtration in the pharmaceutical industry, breweries, wineries, or swimming pools. In addition to stabilizing dynamite, it serves as catalyst support; a filler in paper; paints or plastics; an absorbing agent for oil, grease,

Figure 8 Diatomite exploitation in an open-pit mine at Foufouilloux (Cantal, central France). Frustules accumulated during 50 000 years at a rate of 0.3 mm per year in the 800 × 1300 m lake of an explosion crater formed 5 million years ago. It was then filled with clear, cold, and relatively Si-rich waters that were particularly favorable for diatom growth. Source: Photo P. Richet.



hazardous waste, or in animal litter; a light component in concrete; a soft abrasive in polishing, etc.

From an anecdotal standpoint, one can finally note that the huge variety of diatoms and the specificity of their habitats have led them to be valuable for identification purposes. To quote the single example of forensic medicine, diatoms make it possible to determine whether or not the species found in the lungs of a drowned person are actually those of the water expanse where the body was found even long after death.

3.3 Phytoliths

To begin with mosses, which date back to the Cambrian, phytoliths are produced in most plant groups with the exception of conifers, ginkgo, many cycads, and other gymnosperms [38]. The reason why their shapes are generally specific to the species considered (Figure 4) is that they deposit preferentially in the free spaces of the vascular systems of the plants. Because phytoliths are also found in epidermal cells and in *stomata*, the pores of the leaves or stems through which gas exchange takes place with the atmosphere, coupling of biomineralization with transpiration is commonly assumed [39]. Silicon is in fact the only element that is not toxic for plants at any high concentration. Terrestrial vegetation can accumulate various amounts of this element, ranging from 0.1 to 10% of dry weight depending on whether they reject or accumulate it passively or actively [2]. After having contributed to the rigidity of the plant and its defense against various stresses, phytoliths accumulate in the soil when plants die or leaves fall. Biogenic silica is 7–20 times more soluble in water than silicate minerals. Phytoliths then control the silicon content of porous soil and draining rivers. They improve the quality of soils through clay formation with the silicon species available [40].

From an economic standpoint, particularly important is the silica accumulating in the hard, covering husk (or hull) of rice that protects it against attacks by insects and bacteria. Representing about 20% by weight of the

harvested crop, the husk itself consists of cellulose ($\approx 35\%$), hemicellulose ($\approx 25\%$), lignin ($\approx 20\%$), proteins ($\approx 3\%$), and “ashes” ($\approx 17\%$) whose silica content is about 94% [41]. In view of the 750 million tons of rice yearly produced, the silica obtained could amount up to 25 million tons if the husk were wholly burned. Its main impurities are K_2O , CaO , and Al_2O_3 at levels that can be 1% or higher, depending on soil type, fertilizers used, and climatic conditions [41]. Upon calcination, not only the composition but also the mineralogy and the microstructure of silica obtained depend on possible pretreatments, temperature, duration, and combustion atmosphere. Amorphous silica with a purity higher than 99% and a particle size in the 0.5–0.7 μm range can, for instance, be obtained after leaching the husk with HCl and H_2SO_4 acids [42]. On the other hand, the proportion of cristobalite increases with increasing combustion temperatures whereas trace of tridymite can also be found.

The composition and properties of rice hull ashes (RHA) depend on so many factors that only a few of their uses will be mentioned here. As already noted, they are a potential source of amorphous reactive silica. They have become a starting material for the preparation of silicon and silicon compounds such as silicon carbide and silicon nitride [43]. They are also used for the simultaneous preparation of silica and activated carbon with a high adsorption capacity [44] or as additives in the production of cements where the fine silica particles provide a very compact concrete [45]. The fitness of RHA makes them very good candidates for sealing fine cracks in civil engineering structures. They can penetrate deeper than the conventional cement sand mixture. They also exhibit good thermal insulation properties.

It is also possible to convert silicon dioxide into silicon through a magnesio-thermic reduction process while maintaining the relative morphology of the initial material. Pure Si nanoparticles (SiNPs) can be derived directly from rice husks (RHs) with a conversion yield as high as 5% by mass. Owing to their small size (10–40 nm) and porous nature, these SiNPs are expected to increase the

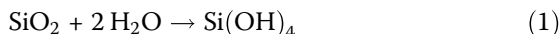
performance of Li-ion battery anodes [46–48]. Taking advantage of the interconnected nanoporous structure naturally existing in RHs, the converted silicon exhibits excellent electrochemical performances. It could provide a theoretical specific charge-storage capacity 10 times higher than that of conventional graphite anodes, which would make RHs a massive resource for the anodes of high-capacity lithium batteries [49]. Finally, biogenic silica particles could also be useful for pharmaceutical purposes as inhibitors of human breast-cancer cell lines and drug delivers for folic acid [39].

4 The Low-Temperature Silica Factories

4.1 Silica Condensation

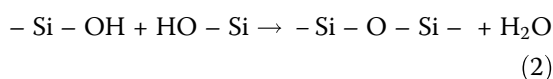
Whether in an aqueous or a terrestrial environment, a major feature of the formation of biogenic silica is the way in which a rather pure silica substance is synthesized from very low concentrations of dissolved silicon species. In shallow sea waters, the total Si concentration is, for instance, a few $\mu\text{mol/l}$ [50], which implies that extremely efficient biological mechanisms have evolved to concentrate silicon species and precipitate them as amorphous SiO_2 .

Silica is slightly soluble in water (0.14 g/l). Under ambient conditions, its dissolution gives rise to silicic acid:

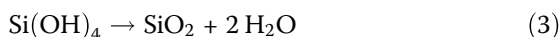


Depending on pH, more or less deprotonated species can then form, ranging from $(\text{H}_5\text{SiO}_4)^+$ at low pH to $(\text{H}_2\text{SiO}_4)^{2-}$ at pH higher than 10.

The reverse reaction occurs upon silica formation. It represents a condensation reaction between two silanol groups leading to the formation of an oxo-bridge between 2 (SiO_4) tetrahedra:



The overall polycondensation reaction can thus be written as:



Small particles form first and then grow in size to yield colloidal solutions (sols) and gels (Chapter 7.5). *In fine* an amorphous SiO_2 , $n\text{H}_2\text{O}$ hydrated silica network is obtained whose nucleation and growth rates depend on the particular physicochemical conditions. The final 3-D network is in particular influenced by factors such as salinity, pH, and, to a lesser extent, temperature [51]. Silica fibers form at low pH whereas colloidal particles

are obtained under basic conditions. These particles are commercially known as *Stöber silica*. Known as *sol-gel* process, these inorganic polymerization reactions are nowadays widely used in the glass industry. Their main advantages over usual melting are to make powderless processing of glasses and ceramics possible, to synthesize highly metastable phases and organic or bio-hybrid materials, and to deposit a variety of amorphous thin films (Chapters 6.8, 8.2, and 8.9).

4.2 Silica Formation in Aquatic Organisms

As a prerequisite to biomineralization, silicic acid must be transported into the cells where condensation might occur. This transfer of silicic acid was first deciphered in the late 1980s through tracer experiments made with the short-lived radioisotope ^{68}Ge to study the expression of a gene coding for a silicon-transporter (SIT) protein isolated from a diatom in ovocytes of *Xenopus laevis* (an amphibian widely used as a model system in biology) [6]. These sodium-coupled active transporters are made up of 10 transmembrane segments. As usually done for characterizing the kinetics of an enzymatically catalyzed reaction, the initial rate transfer is related to the concentration of the substrate and characteristic parameters of the enzyme. These parameters determined *in vivo* for Si transport in different marine and freshwater diatoms point to a high affinity of the SITs for silicic acid with half-saturation constants (K_s) in the 0.2–7.6 $\mu\text{mol/l}$ range. Other mechanisms, such as the transport of the deprotonated form $\text{SiO}(\text{OH})_3^-$ by SITs or the diffusion of $\text{Si}(\text{OH})_4$, have been proposed as alternative routes for the uptake of silicic acid.

Diatoms actually possess multiple SITs. The expression of this multigene family is regulated by the availability and concentration of silicic acid in the medium and by the period of interest during the cell cycle. In this respect, an interesting feature is that similar genes have been identified in other silica-producing species, the *Synurophyceae* algae as well as in the unicellular loricate Choanoflagellates [52]. Such a homology in protein primary structure is thus suggestive of putative transfer of genes both horizontally and vertically throughout evolution.

The formation of silica structures involves organic molecules although complete information on their diversity, concentration, and precise role in the polycondensation process is still missing. In diatoms, several proteins associated with the silica frustules have been identified [7]. *Silaffins* are, for instance, rich in serine ($\text{C}_3\text{H}_7\text{NO}_3$) and lysine ($\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$) amino-acid residues and harbor a high number of post-transcriptional modifications (i.e. phosphorylated, glycosylated, sulfated). Other proteins are also involved in the regulation of the polycondensation process of the valve diatom silica thecae (i.e.

silacidins, cingulins, silicanin, silicalemna-associated proteins). The other kinds of biomolecules embedded within diatoms thecae are long-chain polyamines (LCPA), polysaccharides (i.e. chitin), and lipids.

The morphologically aesthetic but complex biosilica structures formed by diatoms are assembled within the aforementioned SDV. The confinement of amorphous precursors within such specialized membrane-bound compartments allows various features to be controlled: (i) the physicochemical conditions of the polycondensation process (i.e. ions concentration, pH regulation) that are likely to be key issues [53], (ii) the dynamics of incorporation of the organic and mineral fractions, (iii) specific targeting of proteins and molecules to the SDV compartment, and (iv) the 3-D assembly. Several biophysical models have been proposed to explain the regular nanopatterning of biosilica, such as a phase separation process, diffusion-limited aggregation, or even mixed models [54–56].

In sponges, spicules deposit as concentric silica layers around a central proteinic filament. The sponge cells absorb minute traces of silicic acid from sea water and use it to produce a monolithic amorphous silica rod by such a concentric deposition involving an enzyme called silicatein [57]. As already described, small spicules are then extruded from the cell and grow via silica deposition to produce the fibers that serve to anchor the sponge to the deep-sea floor.

4.3 Silica Formation in Plants

The presence of Si within the plant originates in its uptake from the soil in the form of soluble $\text{Si}(\text{OH})_4$ or $\text{SiO}(\text{OH})_3^-$, and then of its controlled polymerization at the final location. Soluble silica from ground water is absorbed by the roots and carried to different parts of the plant by the sap through the vascular system. The first silicic-acid transporter in land plants was identified in a study of a rice mutant (*Oryza sativa*) defective in silicon uptake. The controlling gene, named *Lsi1* (Low-silicon rice 1), which encode a protein belonging to the aquaporin family, is constitutively expressed in the roots. A homolog of this *Lsi1* gene, *Lsi6*, causes the intervascular transfer of Si and is involved in the deposition of silica in leaf blades and sheaths. As also demonstrated in rice, the efflux of silicon from the root cells involves the *Lsi2* gene [58]. After take up, silicon is deposited on cell walls as a polymer of hydrated, amorphous silica to form silica–cuticle and silica–cellulose double layers on the surface of leaves, stems, and hulls. Homologs of *Lsi* genes have been found in several other Si-accumulating plants as diverse as maize (*Zea mays*), barley (*Hordeum vulgare*), sorghum (*Sorghum bicolor*), wheat (*Triticum aestivum*), a

Cucurbitaceae species (*Cucurbita moschata*), soybean (*Glycine max*), and horsetail (*Equisetum arvense*) [59].

Even though Si absorption pathways present similarities in mono- and dicotyledons, our understanding of the protein domains involved in Si-recognition remains rudimentary. Further studies are also needed to address intracellular Si accumulation, subcellular transport, and deposition. We do not know yet when and how the biological cycle of silica evolved. Because it seems to couple with transpiration process and antioxidant activities, however, it should have been an important process for land plants for over 400 My [38].

5 Biomimetism and Applications

Diatom frustules can be considered as novel biofunctional materials, thanks to the large diversity of potentially useful nanostructures in many areas of application [60, 61]. The biomimetic routes investigated involve either the thecae themselves or chemically modified replicates or, alternatively, the use of organic compounds extracted from their biosilica to develop strategies for protein encapsulation or biosensors [62, 63].

Frustules have thus been used for the realization of gas sensing devices based on the photoluminescence (PL) properties of silica, which emits a blue light ($\lambda = 500$ nm) upon UV irradiation at 325 nm. Frustules of a few microns in diameter can be mounted onto the tip of an optical fiber. The position and intensity of the photoluminescent emission peak then depend on the presence of different gases or vapors (e.g. NO_2 , ethanol, or acetone).

Silica frustules have also been used as templates for the realization of 3-D nanostructured materials. The so-called Bioclastic and Shape-Preserving Inorganic Conversion (BaSIC) method was introduced to transform the biosilica frustule into another material while maintaining the original structure. Mesoporous oxides such as MgO , TiO_2 , ZrO_2 , and BaTiO_3 have thus been synthesized with a diatom microstructure. For example, gas/silica displacement reactions, such as magnesio-isothermic reduction, lead to the formation of MgO frustules with fine nanoscale structures. The whole silica frustule can even be reduced into silicon in the form of nanostructured Si materials to open new possibilities in electronics. Insertion of TiO_2 or GeO_2 into the nanostructure is another way that has been proposed to produce LED devices (Chapter 6.9), battery electrodes (Chapter 9.5), or dye-sensitized solar cells [64, 65]. Alternatively, *in vivo* incorporation of foreign elements such as Ge can be obtained upon addition of $\text{Ge}(\text{OH})_4$ to the growth medium of

diatoms. In this way, a homogeneous distribution of Ge atoms is achieved in the silica frustule, providing a typical blue luminescence although one should not lose sight of the fact that germanium is a toxic element for diatoms.

Concerning spicules, yet another of their unique properties is their triboluminescence as discovered in the composite organosilicon materials of *Hexactinellid* sponges. These might contribute to the creation of biomimetic materials capable of emitting light, which, in turn, might be used in various devices for the transformation of energy.

6 Biogenic Silica in the Global Ecosystem

6.1 Silicon Cycle

The silicon cycle in Earth ecosystems is regulated on the one hand by the release of this element upon alteration of silicate minerals and, on the other, by its incorporation in phytoliths on land and in the frustules, spicules, and other silica biominerals in natural waters. On land and at sea, the production of silica is of course tightly related to that of organic matter so that the global cycles of silicon, carbon, and nitrogen are themselves strongly coupled. It, for instance, follows that anthropogenic pressures might in the long-term impact the silicon fluxes from inland waters to coastal systems and, thus, the overall primary biological productivity in these areas. Because of river damming, the concentrations of N and P are, for instance, increasing with respect to that of Si, which could adversely affect diatoms, but the opposite effect of an increased Si flux would result from deforestation, modifications of agricultural practices, and increasing urban populations [2]. Even though it is not easy to estimate the actual balance between such effects, it appears that plant silica plays a key role in connecting the terrestrial and marine carbon cycles.

Of particular importance in this respect are the algae of the phytoplankton, which are at the basis of the most productive oceanic food chains and are also the main agents contributing to the *biological pump* through which carbon is transferred from the surface to the deep ocean. When diatoms die, it was commonly assumed that their carbon content was readily degraded into CO₂ during their fall before reaching depths of about 1000 m. But recent studies have highlighted that the recycling of carbon mainly occurs much deeper at the sediment–water interface. All species do not have the same efficiency in this respect, depending on their size, shape, and Si/C ratios of the frustules and also on their biogeochemical environment. It has nonetheless been estimated that the residence time of carbon at depth is longer than a

century [66]. By comparison, the average residence time of silicon in modern oceans ranges from 15 000 to 17 000 years, suggesting that the silica cycle is currently in a steady state [67].

On a global scale, the contribution of other siliceous protists (i.e. radiolarians, silico-flagellates, etc.) is much less important. But several marine eukaryotic organisms, like siliceous sponges might have an overlooked but non-negligible importance in the Si cycle in specific areas such as continental shelves.

6.2 Silica Versus Calcium Carbonate

The first calcareous deposits known as *stromatolites* began to be made by bacterial colonies 3.7 billion years ago. Ever since the Cambrian (570 My), other biogenic carbonates have been produced in phototrophic, heterotrophic, and autotrophic organisms as diverse as red, green, or brown algae, *cnidaria*, *brachiopoda*, *mollusca*, or *crustacea*, often in close association with chitin [(C₈H₁₃NO₅)_n], a long-chain polymer made up of a derivative of the glucose (C₆H₁₂O₆) sugar. In seawater, the biological formation of either calcite or aragonite, the two main CaCO₃ polymorphs, would not appear to represent a feat. The CO₂ pressure of the primitive atmosphere was, for instance, high and the concentration of Ca²⁺ ions has since then remained high enough in sea water that, with an average value of 0.01 mol/kg, calcium carbonates are actually oversaturated at depths lower than about 2000 m. Precipitation of CaCO₃ polymorphs is not direct, however, but takes place through the dehydration of an amorphous calcium carbonate precursor. That this precursor is usually unstable is not surprising since molten CaCO₃ is not at all a glass-forming liquid. Would it then be possible to interpret the remarkable success of diatoms in terms of the advantages of frustules made up of amorphous silica instead of calcite or aragonite?

7 Perspectives

Climate is not the only factor influencing biological producers of silica. That radiolarians were more abundant in a distant past was probably the result of higher Si concentrations in seawater caused by a strong volcano-hydrothermal activity during periods of major plate-boundary reconfigurations. The ubiquitous nature of diatoms and their predominance in cold and turbulent waters of the oceans has long been established, thanks to their particularly efficient way of handling the aqueous silicon species available at a low energy cost. Except in Austral seas, this predominance might be threatened if warmer and stratified oceans were to prevail in the future.

In that case, however, one cannot exclude that diatoms would be able to adjust successfully to new conditions that would include more acidic waters.

As a matter of fact, much remain to be learned concerning not only the synthesis of biogenic silica, but also the way in which their producers interact with their environment or how the silica-armored preys and their predators coevolved. At a most fundamental level, the manner in which Si transporters have evolved has still to be deciphered. It nonetheless appears that both SIT and Lsi2 transporter families are found in different lineages, which suggest that they originated in a distant Precambrian past when oceanic Si concentrations were much higher than today [68]. It has thus been surmised that Si transporters might have first evacuated toxic Si at high concentrations from the cells before serving instead a biomineralizing role. However, the true role of silicification in cell detoxification might need deeper investigations. Silicon transporters might have not only various origin (e.g. aquaporin-related sequences in plants and humans, and SIT-related sequences in fresh and marine water diatoms, chrysophytes, silicoflagellates, dinoflagellates, haptophytes, ciliates and choanoflagellates, and in bacteria), these transporter families might have been acquired independently, but also suffered lost in several lineages, duplication, and sub-functionalization events. Therefore, a better understanding of the evolution of silicon transporters and of the expression and regulation of these genes is likely to have significant implications on our understanding of the capabilities of these organisms to cope with environmental changes, and implicitly on the human impacts on several biogeochemical cycles.

In materials science, biogenic silica has opened wholly new areas. Beginning with a few pioneering studies three decades ago (e.g. [69]), rice-husk valorization has, for instance, become a very active field of research. Another rapidly expanding domain is that of bioinspired glasses. As already noted, porous diatom frustules can, for example, be used as precursors for the production of nanostructured materials such as photonic crystals. On the other hand, sol–gel processes are already extensively used industrially in many applications such as the production of coatings, fibers, and nanoparticles (Chapter 8.2). The *soft* conditions associated with the production of these glasses have led to the design of hybrid organic–inorganic materials in which both organic and inorganic species can be mixed at a molecular level ([70], Chapter 8.9). A further development already under way consists in trapping biomolecules such as enzymes or even whole cells within these new materials to form “living materials” [71, 72] but there is little doubt that this approach will give rise to unexpected new products and processes in the next decades.

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8.2

Sol-Gel Process and Products

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1 Introduction

To synthesize amorphous or crystalline materials at relatively low temperatures, sol-gel methods are based on colloidal chemistry processing, involving the preparation of a colloidal suspension (sol), the gelation of the sol, and the removal of the liquid existing in fine interconnected channels within the gel. The product is then dried, for instance, at a temperature as low as about 100 °C. The dry gel is still porous, so it must be finally sintered at a temperature close to the glass transition (T_g) if a dense glass is to be produced, or it can be used in the form of a porous material.

This technology is an alternative to traditional melting and quenching for glass preparation that is especially suitable for the deposition of coatings. But the sol-gel technology can also be used for the fabrication of glasses in bulk, nanoparticle, powder, or fiber forms, which have structures virtually identical to those of melt-quenched glasses of the same compositions. The process is used to prepare ceramic materials as well, which include one or more crystalline phases. Some of these may be glass-ceramics obtained by the controlled crystallization of sol-gel-derived glasses [1].

The sol-gel process can claim a long history since the first (casual) observation of the hydrolysis and polycondensation of silicic acid dates back to the work of Jacques-Joseph Ebelmen (1814–1852) in 1846 [2]. But practical use of such reactions had to wait almost a century when Geffcken and Berger in 1939 synthesized SiO₂ glass layer glass from gels [3], whereas the first multicomponent silicate sol-gel glasses were prepared by Della and Rustom Roy in 1955 [4]. The growing interest of many researchers in the method became apparent only

in the mid-1970s, however, particularly when the work of Dislich [5] opened new synthesis routes of oxide glasses and thus triggered an ever-growing number of potentially attractive applications. Considering the preparation of multicomponent oxide glass coatings on suitable substrates, with application such as protective layers against oxidation and weathering, the first commercial products were probably automotive glass coatings (antireflective) developed by Schott Glass Works in the 1950s, based on alternating silica glass and titania sol-gel-derived layers. This expansion was also fostered by the decreasing cost of precursor chemicals, which was one of the initial impediments to many applications, as well as by increasingly reproducible processes.

At present, sol-gel processing is used to prepare a large number of amorphous and glassy materials, particularly functional coatings for many different purposes, as well as other types of inorganic and *hybrid* (organic-inorganic) coatings on glass, sometimes partly or even fully crystalline, and aerogels (Chapter 8.3). Many companies utilize it nowadays even when it is not their core business. Some of the important industrial companies in the field include Schott (Germany), the Donnelly Corp. (USA, optical coatings), Denton Vacuum Inc. (USA, optical coatings), Aspen Systems (USA, aerogels), Geltech (USA, optical components, porous substrates, and powders), Hybrid Glass Technologies (USA), and Nanogate Technologies (Germany), specialized in hybrid sol-gels, SIMAX Technologies (USA, fiber optics, microlenses, etc.), Sol-gel Technologies (Israel, health care products), and Chemat Technology Inc. (USA, precursors and processing equipment).

In this chapter, we will thus begin with details of the most representative sol-gel chemistry and forming processes, concerning the most important inorganic and hybrid materials that are currently prepared. We will then summarize the main advantages and drawbacks of the process at present, before describing products and applications, from

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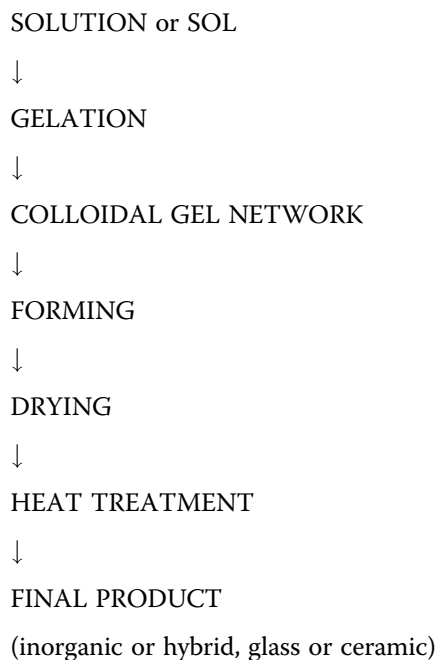
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zero-dimensional (0-d) nanoparticles to 3-D bulk glasses and finally pointing to new features of sol-gel science and technology that are likely to gain momentum in a near future.

2 Sol-Gel Processing

2.1 Basics of Sol-Gel Processes

Conversion of a solution or a sol into a dense material requires the following steps:



Sintering is not included in this flowchart because it is an optional step, necessary for making eventually a glass, but occasionally absent, particularly when organic groups are designed to be present in the final (hybrid) product (Chapter 8.9). The chemistry consists of reactions involving colloidal particles in a sol, or between alkoxide-derived polymeric species and water in a solution, leading to a highly porous amorphous gel network, where a liquid phase (solvent, catalyst, and eventually excess water and precursors) may be retained. During drying and sintering, the open network typically undergoes at least 50% linear shrinkage caused by removal of the liquid phase and drastic reduction of the porosity, ultimately forming a dense sol-gel material (inorganic glass or ceramics). Depending on several interrelated experimental parameters, a wide range of microstructured products may be obtained (Figure 1). These include (i) inorganic or hybrid coatings on a substrate, for which the process is a highly convenient technique that starts at ambient temperature and pressure; (ii) hollow, dense, porous, or structured nanoparticles; (iii) high-purity powders from which

dense ceramics can be obtained via sintering; (iv) very low-density aerogels obtained by supercritical drying of wet gels and rather difficult to prepare by other techniques; (v) and fibers, which can also be fabricated, although the technology is not the best available in this case.

2.2 Inorganic Sol-Gel Materials

In the *colloidal route*, colloidal particles are formed in an aqueous medium from ionic species according to the principles of colloidal chemistry. In the case of silica, for example, the ~1 nm SiO₂ particles present in sols of dilute silicic acid undergo rapid growth up to 2–4 nm at pH 2–3. As described below, the silica solubility increases so much above pH 7 that the particles grow up to 4–6 μm by coalescence and Ostwald ripening. Monomeric silicic acid then helps cementing the nanoparticles to form a bulk gel.

The most common synthesis process, however, involves the *polymeric route*, which may also be exemplified with silica. Here, metallic salts, metal alkoxides, or other more complex organometallic precursors undergo hydrolysis and polycondensation to form the gel. Because of the hydrophobic nature of the alkyl groups, organometallic precursors and water are not miscible, so that addition of a common solvent (usually an alcohol) becomes mandatory to promote miscibility between the reactants. In the most common case where an alkoxide is used as precursor, the alkoxide molecules in solution undergo hydrolysis, usually with the help of a catalyst, either an acid or a base.

Acid catalysts – usually HCl, HNO₃, or CH₃COOH – are thought to promote hydrolysis by electrophilic attack. The rate of hydrolysis increases with the decrease in pH, starting from 7; meanwhile, the condensation reaction rate exhibits a local minimum at the silica isoelectric point at pH 2. Acid-catalyzed sols exhibit longer gelling times than base-catalyzed ones, yielding gels with a large volume shrinkage. When a base, such as ammonia, is selected instead as a catalyst, hydrolysis takes place by nucleophilic attack and progresses slowly, while silicate monomers start condensing before being fully hydrolyzed. Base-catalyzed products generally shrink less than those synthesized under acidic conditions, thus being lower density products.

The hydrolysis is followed by water and/or alcohol forming condensation reactions (Figure 2). Hydrolysis and condensation occur simultaneously rather than sequentially; in fact, Si–O–Si (siloxane) bonds have been observed immediately after the addition of water and catalyst to the alkoxide solution, suggesting that condensation is initiated as soon as the first alkoxy group has been hydrolyzed. The initial condensation is quite fast, within minutes or less [6], although it slows down as

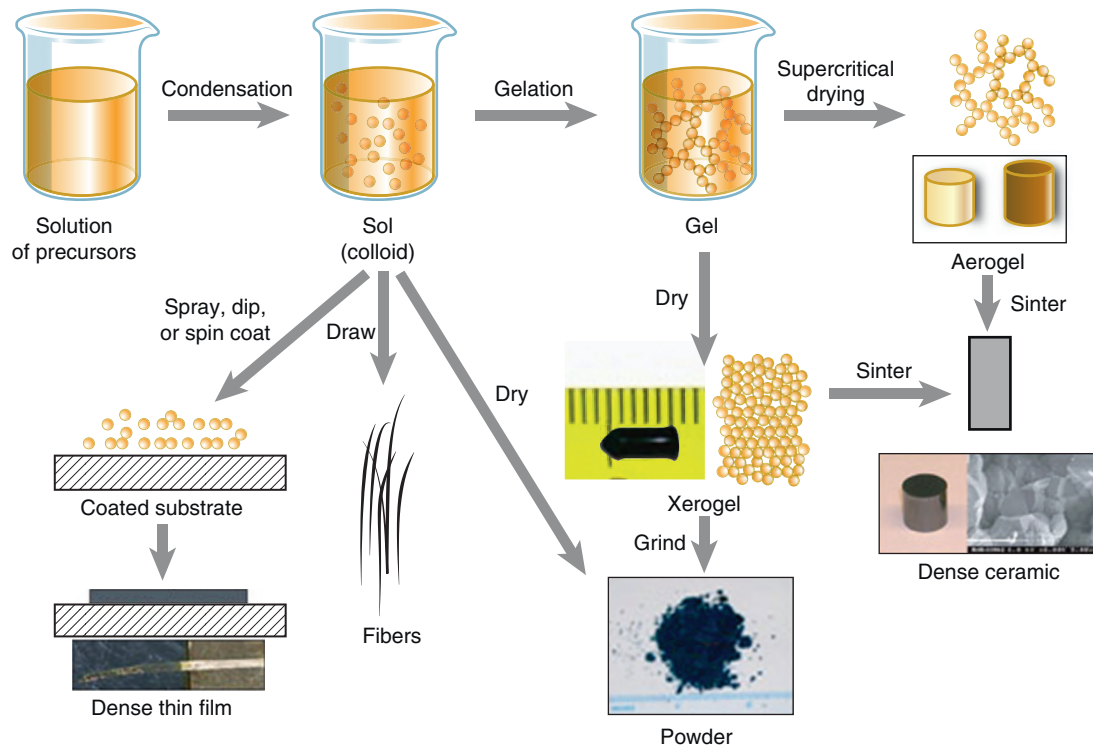


Figure 1 Range of products that can be prepared via sol-gel processing.

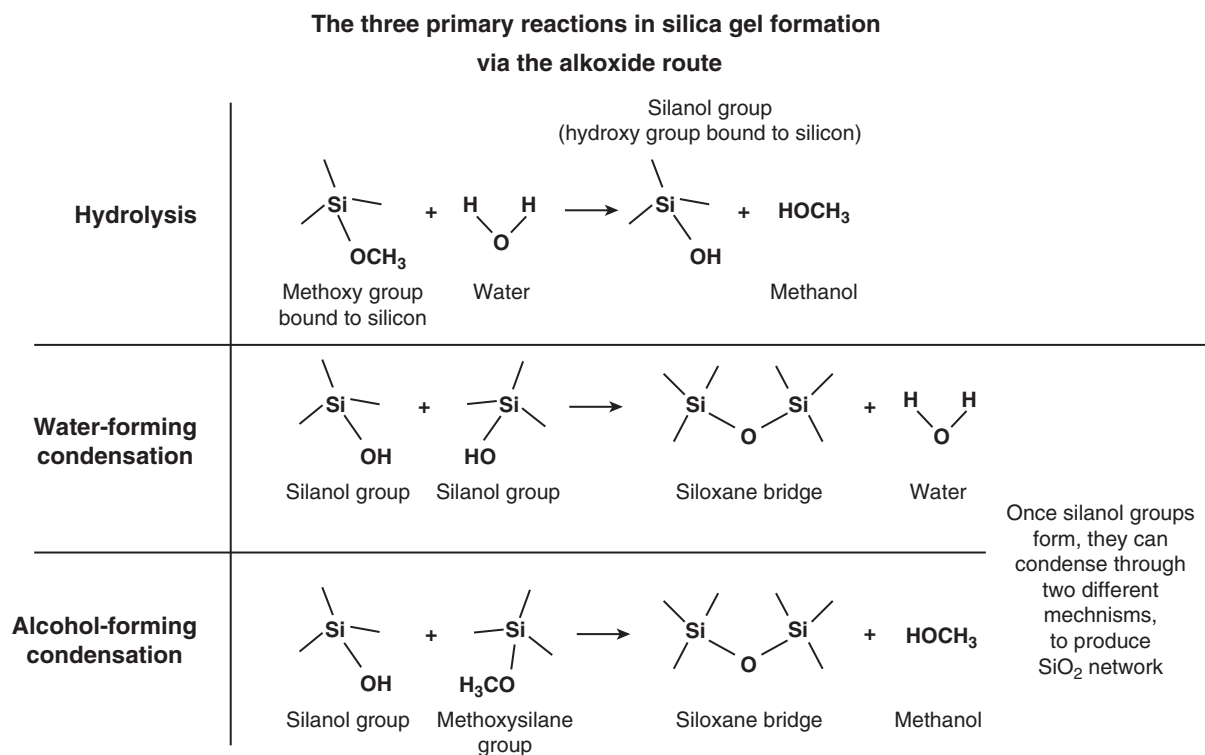


Figure 2 Alkoxide sol-gel reactions: hydrolysis; water- and alcohol-forming condensation.

polymerization progresses. For $\text{Si}(\text{OC}_2\text{H}_5)_4$, tetraethyl orthosilicate (TEOS), the most popular silica precursor, the time for hydrolysis completion is less than 10% of the time for gelation under acid-catalyzed conditions.

The pH plays a critical role in all processes. Particularly at values lower than 3, complete hydrolysis, whereby four moles of water are consumed per mole of TEOS, produces linear or highly branched polymeric species that have a fractal structure and nanopore diameters lower than 2 nm. As the pH increases toward 7, dissolution and condensation reactions become relevant, promoting Ostwald ripening or coalescence and enhancing the coarsening of the structure. Above pH 7, the growth rate of particles is maximum because an increasing silica solubility promotes depolymerization of siloxane bonds. In turn, the monomeric silica produced helps the aging process through an Ostwald ripening-coarsening mechanism that yields mesopore diameters of well above 2 nm.

For the synthesis of multicomponent gels, the polymeric solution route offers great possibilities. The miscibility of different alkoxide compounds allows in principle complete polymerization of all metal species to be achieved and, thus, highly homogeneous products to be synthesized. This principle notwithstanding, the distinct rates of metal alkoxide hydrolysis may cause heterogeneities and phase separation in the final gel. If two different metal-alkoxide precursors are used, however, a sequential addition process, by which the least-reactive alkoxide is pre-hydrolyzed to some extent before the more reactive is added, tends to prevent heterogeneities from appearing. In this way the two metal species can be placed randomly along the polymer chain. As an example, the

flowchart for SiO-TiO_2 synthesis is shown in Figure 3 where Ti isopropoxide (TIPOT) is the source of titania, the catalyst is acetic acid and ethanol (EtOH) the solvent; the composition of these products can vary all the way from pure silica to pure titania. Ultra low-expansion glass, a registered trademark of Corning Inc. (ULE[®]), is one such example. Displaying a very low coefficient of thermal expansion of about 10^{-8} K^{-1} between 5 and 35 °C, ULE is composed of silica and less than 10 % titania. Sol-gel zirconia powders are another example of how solid-state allotropic phase transitions may be suppressed by a colloidal chemistry approach.

In sol-gel film deposition, the most common methods used to ensure fast drying of the solvent are dip- and spin-coating (Figure 4). With the former, a substrate plate is immersed in the sol and slowly withdrawn at a constant rate of the order of $\sim 1\text{--}30 \text{ cm/min}$, while drying at the meniscus leads to the progressive deposition of a thin film on the substrate; the faster the withdrawal, the thicker the film obtained, which can reach several microns. This method is especially suitable for coatings on large surface areas, for example, on glass windows. In the spin-coating process, the sol is dispensed on top of a horizontal substrate, which is then rotated at high speeds of the order of 1500–3000 rpm, for short times of $\sim$ about 20–30 seconds. Spin-coating allows the deposition of films on one side only of substrates of surface areas of up to $\sim 1 \text{ m}^2$. A high-quality thin film is deposited through quick elimination of the excess liquid by fast evaporation. The electrodeposition (or electrophoretic deposition) method is also used, for example, to coat metallic substrates, but less frequently. Depending on their charge, the particles (in a sol) or the polymers (in a solution) move in a direction opposite or parallel to an applied external electric field and then are deposited on the piece to be coated, which serves either as the cathode or the anode.

A variety of substrate geometries may be accommodated. After the gel film is dried, it can be sintered at a temperature near T_g into a dense glass. Depending on the actual deposition method used and on the viscosity of the precursor sol, the thickness of a single layer of inorganic films may vary from a few tens up to $\sim 300\text{--}400 \text{ nm}$. If thicker layers are sought after, multilayered films may also be prepared, several microns thick, through a sequence of dip- or spin-coating and rapid intermediate thermal annealing steps. Additional possibilities also arise if the substrate has previously been micro-patterned because a multitude of structures with different shapes and architectures can be fabricated, thanks to the wide range of designs offered by soft lithography. As a matter of fact, coatings are immune of the bubbles and carbon particles that result from incomplete hydrolysis and are usually difficult to eliminate in monolithic products. Because processing is much easier for coatings than for

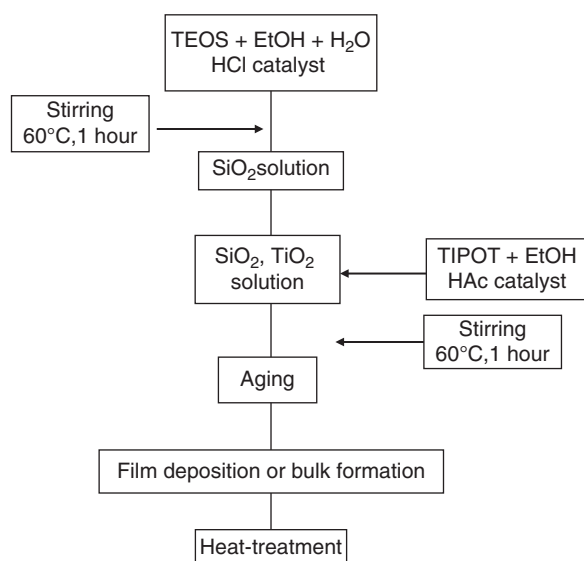
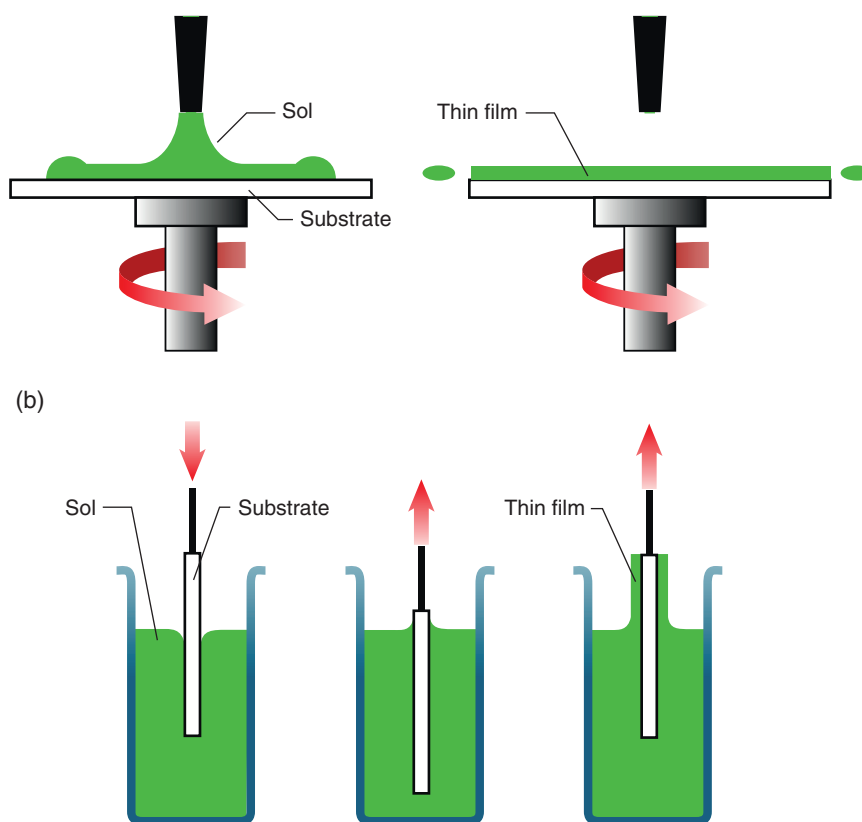


Figure 3 Flowchart of the silica-titania sol-gel process, with $\text{pH} \leq 2$.

Figure 4 Sol-gel film deposition methods: (a) spin-coating and (b) dip-coating.



monoliths, about 10 m^2 of flat defect-free glass films have already been produced.

2.3 Hybrid and Other Sol-Gel Materials

Incomplete structural relaxation during drying is a central problem when it comes to produce monoliths or thick films. If the stress caused by capillary forces within the gel pores exceeds a certain critical value, cracks will appear either during drying, especially in monoliths, or during the final densification in thick films. Several approaches have been proposed to overcome this inherent weakness. In the late 1970s, organic groups such as $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, and $-\text{C}_{11}\text{H}_{24}\text{O}_4$ began to be incorporated into the gel network within which bonding was made possible by the non-hydrolyzable $\text{Si}-\text{C}$ bonds of the precursors. This procedure gave rise to the so-called ORganically MODified SILica materials, known as ORMOSILS [7], which belong to the general category of hybrid (organic/inorganic) materials. The presence of the more compliant organic groups, together with the eventual cross-linking between hybrid polymeric chains, allows mechanical properties to be tailored and stress to be dissipated by plastic deformation.

For example, ORMOSIL materials combine the mechanical strength, chemical resistance, thermal stability, and optical transparency of glasses and ceramics with the toughness, flexibility, and lightweightness of organic polymers. Further, network porosity and surface chemistry can be tailored to the designed performance. These materials have even a higher versatility than silica: the presence of organic groups not only makes them more flexible but it also allows wettability to be adjusted by a judicious choice of the ratio of hydrophilic ($\equiv\text{Si}-\text{OH}$, $\equiv\text{Si}-\text{O}-\text{Si}\equiv$) to hydrophobic ($\equiv\text{Si}-\text{R}$) groups. The hybrid materials are usually processed at the fairly low temperatures of about 200°C at most for a couple of hours, in order to preserve the organic species, so they are ideal for coating plastic substrates.

Supercritical drying is another possible method to avoid gel shrinkage. Here, the liquid is removed through drying above its critical point so that no capillary stresses develop since no liquid-vapor interface exists. The resulting gel, named *aerogel*, has a volume similar to that of the dried wet gel, with a huge residual porosity (Chapter 8.3). This causes the aerogel materials to be, for example, extremely good thermal and sound insulators.

Sol-gel materials with a tailored porosity are other interesting products. After the seminal work conducted

in the early 1990s by researchers at the Mobil Oil Corporation [8], surfactants such as Brij56™, C16TAB, or C12TAB (lyotropic liquid crystalline phases) have been used as templates for sol-gel materials. One of the advantages of using homogenous phases as templates is that the nano-architecture of the reaction mixture is retained throughout the condensation and gelation processes so that the nanostructure of the material can be determined *a priori*. Thin films of nanostructured mesoporous silica, for example, are of interest for a range of applications, in particular for medicine and integrated sensors.

3 Advantages and Drawbacks of the Sol-Gel Process

The sol-gel process has many advantages over conventional melting-quenching techniques, especially in terms of improved purity and lower fabrication temperatures. However, difficulties related to the production of large, dense monoliths and to the cost of the starting materials still persist. These advantages and drawbacks over the classical melting-quenching technique are thus summarized in Tables 1 and 2.

4 Sol-Gel Products and Applications

The dimensionality of current types of products ranges from 0 (nanoparticles), to 1 (fibers), 2 (coatings), and 3 (bulk glassy materials). In this chapter, we will restrict ourselves to products and applications where glass is involved as the sol-gel material, or, at least, as the substrate.

4.1 Nanoparticles

Inorganic and hybrid sol-gel micro- and nanoparticles (Figure 5) have attracted much attention in recent years within both the academic and industrial communities. In addition to their huge surface-to-volume ratio, favoring miniaturization, nanoparticles give rise to unique optical, electronic, and magnetic properties, depending on their size, shape, and composition.

Nanoparticles may exhibit a wide range of geometries – from spherical to tubular, through centric, eccentric, and star like – may be plain or nanostructured – core-shell or porous structured – have different sizes and shell thicknesses, be hollow, differ in crystallinity and surface morphology, and finally be fine-tuned relative to one or more properties. Furthermore, they can be functionalized in

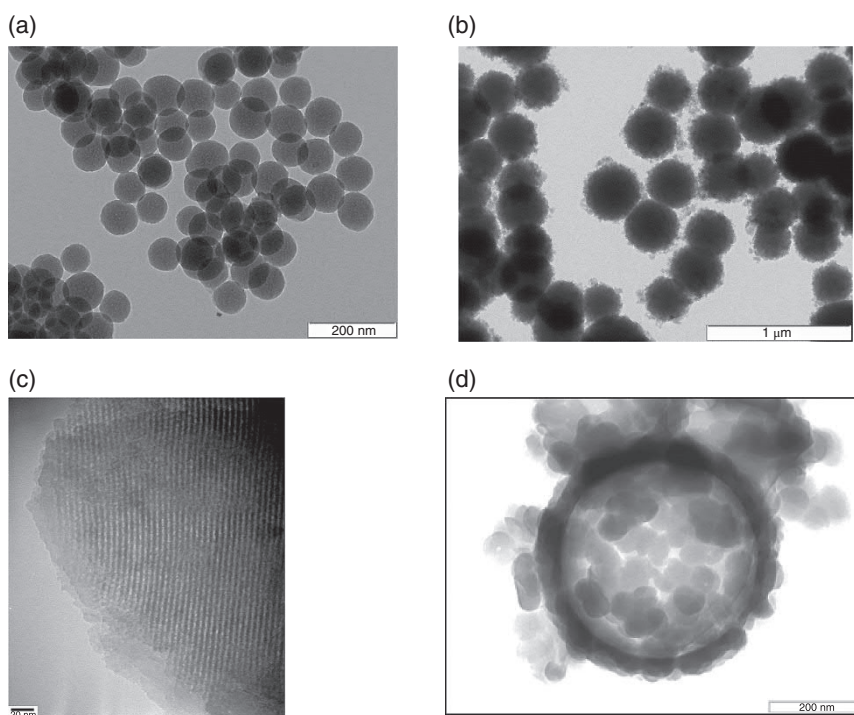
Table 1 Advantages of the sol-gel process.

Advantages	Comments
1. Formation of homogeneous noncrystalline solids in original composition ranges	One of the main advantages of SG processing lies in the possibility of preparing new glass compositions that would otherwise undergo liquid-liquid unmixing or crystallize upon quenching of a high-temperature melt.
2. Formation of new metastable crystalline solids with unusual compositions	Possibility of precipitating crystals that do not form at higher temperatures because of either slower kinetics or greater metastability than other crystalline forms or assemblages.
3. Special products, such as nanoparticles, films, and fibers	For films, possibility of low-temperature coatings not affecting the stability of the substrate. Dense, hollow, or core-shell nanoparticles, either inorganic or hybrid, may be obtained.
4. Improved homogeneity	Multicomponent oxides with a well-defined stoichiometry, or doped, may be prepared from different chemical precursors, even if the SG kinetics of the different precursors must be carefully controlled to produce the designed multicomponent composition with the required level of homogeneity. Mixing of the precursor solutions at the molecular level ensures an extra degree of homogeneity.
5. Improved purity	Another significant advantage lies in the outstandingly high purity of the final products. The use of liquid precursors containing less than 100 ppb of total metals, such as orthosilicates, together with solution handling at room temperature without any contamination from the container, guarantees the very high purity of typical SG products.
6. Low-temperature preparation	Owing to their high surface energies, colloidal particle compacts sinter well below their thermodynamic melting temperatures, whose actual values depend on the particle size, shape, or composition, or near the T_g of their melt-quenched glass counterparts. Low sintering temperatures not only mean lower energy costs but also contribute to the purity of the final product, which is free of contamination from refractory-lined furnaces. This is particularly important for silica glass, which needs to be melted well above 2000 °C.

Table 2 Drawbacks of the sol-gel process.

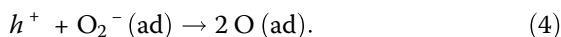
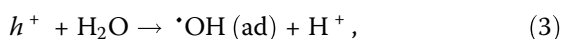
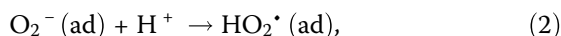
Disadvantages	Comments
1. Raw materials costs	Most precursors have a relatively high cost, despite a continuing decreasing trend, such that the SG process is more suitable for specialty glass products, where raw materials' cost is not critical, than for large-scale production. For example, the raw materials' costs for 1 ton of sol-gel silica are ~47 000€, against ~200€ when produced by traditional melt/quenching of high-purity silica sand. It is therefore unlikely that high-volume glass products like flat glass, container glass, cooking ware, and common fibers will be produced by the SG technology.
2. Large shrinkage during processing	SG products have a high pore volume where solvents and eventual excess reagents may be trapped. The complete removal of the liquid phase and elimination of porosity during drying and sintering causes a significant degree of shrinkage of the final SG product compared to the initial wet gel, particularly for monoliths and thick films, which complicates near-net shape design.
3. Residual hydroxyl groups and carbon	Hydroxyl and carbon residues (the latter mostly in monoliths) are difficult to eliminate completely.
4. Health hazards of organic solutions	Continuous or isolated exposure to organic solvents may cause: I. Acute poisoning Narcosis; irritation of throat, eyes, or skin II. Chronic poisoning Liver and kidney damage; blood damage; nervous system damage Alcohols in particular, besides being anesthetics, may cause irritation of the eyes and upper respiratory tract.
5. Long processing times	This is a problem with monolith fabrication, but not with thin films. The deposition of thick multilayer films is more time-consuming.
6. Difficulty in producing large pieces	Again this concerns monoliths; the deposition of large area coatings usually presents no problem.

Figure 5 Transmission electron microscopy images of sol-gel silica nanoparticles: (a) inorganic dense NPs, (b) ORMOSIL dense NPs, (c) inorganic nanostructured NPs (templated with Brij₅₆), and (d) inorganic hollow-nanosphere (dark circle in the figure).



situ and further conjugated with a wide range of small ligands (usually organic) and/or large biomolecules. This connection with biomolecules through bonding of a protein, a peptide, an antibody, or other molecules makes possible to target a nanoparticle to specific sites in the organism, in particular to specific cellular receptors [9].

Additionally, nanoparticles enable the encapsulation and controlled release of various substances (e.g. drugs, biomolecules, cosmetics, dyes, and inks) and may enhance a catalytic action. Its high photocatalytic efficiency, thermodynamic stability, and low cost make titanium dioxide (TiO_2) the prime candidate for photocatalytic use at an industrial scale [10]. Such TiO_2 nanoparticles may, for instance, decompose pollutants by reactions (either oxidation or reduction) photocatalyzed at their surface. The different forms of active oxygen produced – O_2^- , $\cdot\text{OH}$, $\text{HO}\cdot$, and $\text{O}\cdot$ – cause polluting agents, either organic or inorganic to break down according to the following reactions [11]:



where e^- designates an electron, h^+ a photon, and (ad) indicates an adsorbed species.

Another advantage is that the nanoparticles can be nanostructured in situ through the use of surfactant templates or may even be made hollow [12, 13] (Figure 5c and d, respectively). Finally, nanoparticles can be multifunctional, i.e. be capable of accomplishing multiple objectives such as serving for imaging and delivering drugs (*theranostics*), or performing a single advanced function through incorporation of multiple functional units. For biomedical applications, an appropriate size range (~10–200 nm) and a mono-sized distribution are normally required for effective operation. Inorganic or hybrid sol-gel coatings can also be combined with a wide range of core materials in core-shell nanostructures.

As exemplified by SiO_2 nanoparticles, the classical aqueous route comprises two main alternatives: the microemulsion process (or reverse microemulsion) and Stöber method. In the first case, a reverse-micelle or water-in-oil microemulsion system is formed by mixing water, oil, and surfactant. The reactions take place in the dispersed aqueous phase, forming confined reaction vessels. The nucleation and growth kinetics of silica nanoparticles are highly conditioned by the size of water droplets in the microemulsion system, while the surfactant coating prevents agglomeration and enhances the nanoparticle colloidal stability. Dynamic adsorption and desorption of surfactant molecules at the nanoparticle

surfaces during growth, particularly the selective adsorption toward crystal faces, enables one to control the nanoparticle size, size distribution, and morphology. In the procedure described by Stöber et al. [14], SiO_2 nanoparticles are produced by hydrolysis of an alkoxide precursor such as TEOS in an ethanol solution, under basic catalysis. This hydrolysis starts producing silicic acid, which condenses to form highly porous amorphous nanoparticles. The Stöber method is a room-temperature, surfactant-free route that ensures an eco-friendly synthesis of nano- or microparticles, with diameters comprised between 30 nm and 2 μm [15].

Aqueous sol-gel chemistry may nonetheless be complex when it comes to nanoparticle synthesis. The difference in reactivity of the metal oxide precursors, the competition between hydrolysis and condensation reactions, and possible aggregation or Ostwald ripening may prevent the nanoparticle size, size distribution, and morphology from being controlled. Additionally, the as-synthesized oxide nanoparticles are often amorphous and the final crystallization process may harm process reproducibility. Although much less popular, another chemical route to produce oxide nanoparticles is nonaqueous. Here, no water is present, the oxygen being provided by solvents such as ethers, alcohols, ketones, or aldehydes, or by the organic constituents of the alkoxide or acetylacetone precursors [16].

4.2 Coatings and Thin Films

Whereas fibers are still not very common, coatings and thin films are, by far, the most important category of products and applications at present ([17], Chapter 6.8). Many of these coatings exhibit several functional properties obtained via easy and fast processing. Those considered here may be glassy films on a glass or another type of substrate, or at least partially crystalline films, but deposited on glass substrates. For such products and applications, either inorganic or hybrid materials are utilized, the latter having the advantage of low-temperature post-processing by UV irradiation or heat treatment made online after a deposition step often made with standard industrial technologies. The main categories may be divided into the following six applications: (i) automotive, (ii) architectural, (iii) ophthalmic, (iv) electronic, (v) household, and (vi) optical.

In the category of automotive coatings, head-up displays are becoming common in some cars in the high-end of the market. Based on silica-titania films, they allow drivers to read information on the rear-view mirror or on the inside surface of the windshield without having to watch off the road (Chapter 9.2). Besides, water-repellent (hydrophobic) and abrasion-resistant transparent coatings for automotive windows may, for example, be micro

phase-separated silica-titania films (from silica precursors like MTES, methyltriethoxysilane). There are also colored coatings for tinted automobile windows as well, based on different transition metal oxides dispersed into silica films.

Architectural products (Chapter 9.1), on the other hand, include solar-control coatings reflecting both the near ultraviolet and near-infrared components of the solar spectrum, self-cleaning (photocatalytic) titania coatings for glass windows, or electrochromic coatings for glass windows in buildings, which change color by means of an applied electric field. Besides, dichroic windows for building display beautiful variable colors because they display interference effects from alternating multilayer stacks of high/low refractive index materials like titania ($n \sim 2.2$) and silica ($n \sim 1.46$).

Similar applications are found for ophthalmic products. Antireflection and (hard) anti-scratch hybrid coatings cured at low temperatures are, for instance, used for plastic eye lenses. The former may be optical thin films of low refractive index ($n < 1.30$). These are, for example, obtained with an MgF_2 - SiO_2 mixture where the presence of the light element F lowers the density, and thus the index of refraction.

In the area of electronics, antireflection coatings are extensively used. Transparent conducting oxide coatings like ITO (Indium-Tin-Oxide, $\text{In}_2\text{O}_3 : \text{Sn}$), or ATO (Antimony-Tin-Oxide, $\text{SnO}_2 : \text{Sb}$), serve as electrodes for various applications such as solar cells, display glasses, sensors, and electrochromic windows (Chapter 6.10). Other transparent conducting oxide coatings are deposited in glass tubes for antistatic properties, for example, in flow meters. Mention should also be made of the “spin-on glass,” which designates a silica-based sol for

the planarization of electronic integrated circuits and has become an important product available worldwide.

Examples of household applications are the antifogging hydrophilic coatings, based on SiO_2 - ZrO_2 layers deposited on glass windows and mirrors, for example, in bathrooms, where the introduction of zirconia decreases the wettability of the silica films.

Coatings for optical devices include antireflection coatings of high-performance lenses with the aforementioned MgF_2 - SiO_2 mixture. Likewise, such coatings with a high laser damage threshold are made up of porous silica films for potassium dideuterium phosphate crystals in frequency-doubled lasers, as well as for glassy optical waveguides and waveguide sensors (such as biosensors).

Another interesting application concerns sol-gel-derived photonic crystal coatings like Bragg mirrors for solar control (already mentioned as an architectural product), Fabry-Perot microcavities for white-light generation applications [18], and opal/inverse opal coatings for strain sensors [19], of which two examples are shown in Figure 6. Like dichroic windows, Bragg mirrors consist of alternating multilayer stacks of high/low index materials but in their microcavities the mirror periodicity is interrupted by a double thickness defect layer, which may be doped for white light generation with active elements such as lanthanides. The synthetic opals and inverse opals are derived from self-assembled close-packed arrangements of dielectric spheres. Another category of coatings that do not belong to the previous ones are the wide variety of inorganic and hybrid films, for example, made up of ZrO_2 -, TiO_2 -, Al_2O_3 -, or CeO_2 -bearing silicates, which are used for protecting metals such as steel.

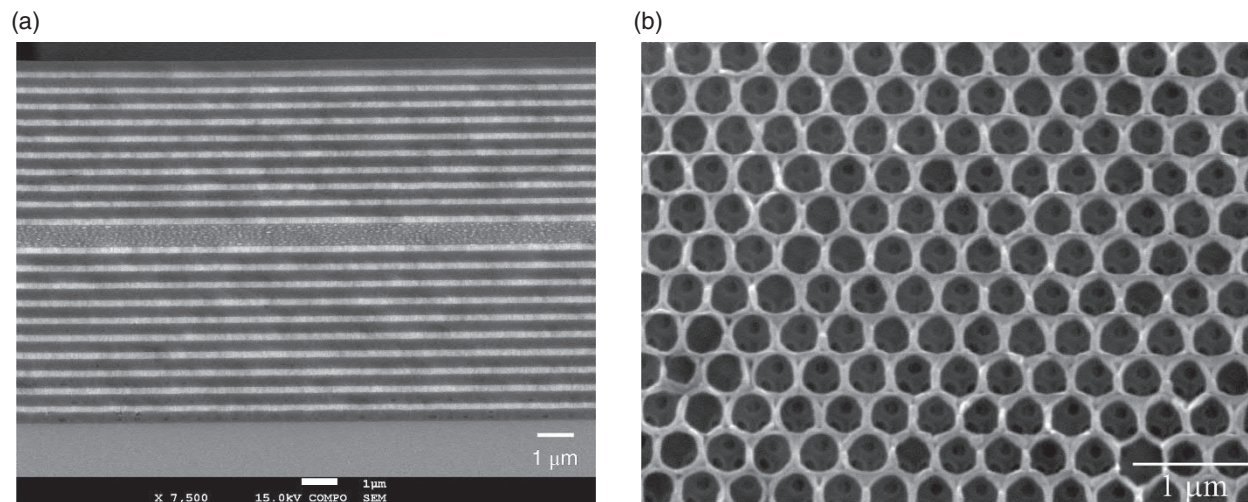


Figure 6 Examples of sol-gel prepared photonic crystals: (a) Fabry-Perot microcavity of alternating high/low index films for white light generation; (b) titania inverse opal for sensing. (Both (a) and (b) are scanning electron micrographs).

4.3 Bulk Sol-Gel Products

Bulk sol-gel products include the cladding tube of fiberoptic preforms (Chapter 6.4), essentially made of base-catalyzed silica, gradient index rods based on Ti leaching from (SiO_2 -rich) silica-titania glass rods, or membranes with tailored porosity for separation and filtration or other applications. Of interest are also high-performance-liquid-chromatography (HPLC) column fillings based on porous silica monoliths with a bimodal meso/macroporous ($\sim 0.1\text{--}40\text{ }\mu\text{m}$) pore size distribution. They are prepared by hydrolysis and polycondensation of alkoxy silanes in the presence of water-soluble polymers, which leads to polymer-induced phase separation [20]. Another interesting application of the concept of bimodal pore size materials is nano/macroporous scaffolds for bone tissue regeneration ([21], Chapter 8.4), such as calcium phosphosilicate glasses shown (Figure 7). Sol-gel glasses have also been suggested as a possible matrix for nuclear waste encapsulation as an alternative to borosilicate glasses (Chapter 7.6) because of the advantage of low-temperature sintering compared to high-temperature melting and also of the possibility of incorporating a wider range of radioactive elements. Finally aerogels, thanks to the extremely large porosity associated with a density of $\sim 0.1\text{ g/cm}^3$ for a typical silica composition, have thermal conductivities lower than 0.02 W/mK and are thus used as highly efficient thermal insulation materials, as well as in sound insulation and Cherenkov (γ -ray) detectors. The upper temperature limit for use in thermal insulation is $\sim 1000\text{ }^\circ\text{C}$.

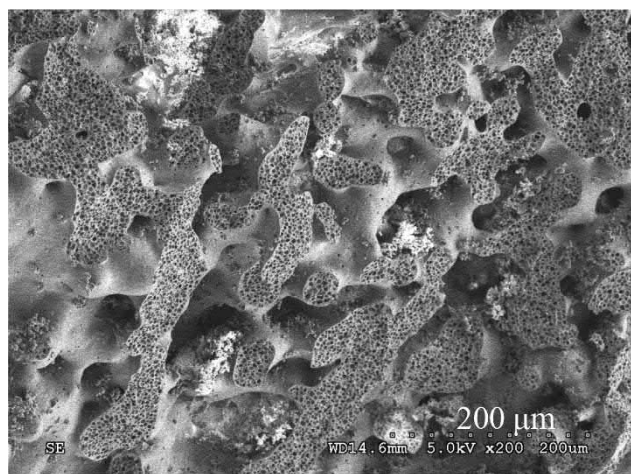


Figure 7 Scanning electron micrograph of nano/macroporous scaffold for bone tissue regeneration obtained from sol-gel 60 SiO_2 -36 CaO -4 P_2O_5 (mol %).

5 Perspectives

The sol-gel technology is a field that has been expanding at a very significant rate. However, the fact that its applications are largely dominated by coatings means that the material produced is often only a component integrated within a larger product whose fabrication may involve several other technologies. For the electronic industry, spin-on-glass films with different functionalities are a good example of this paradigm, which may ultimately affect the visibility of many sol-gel products. One of the most attractive features of the sol-gel process is that it may produce materials with compositions that cannot be obtained with conventional methods. One can thus expect quite new glasses to be created in the future, even if only as thin films, thanks in particular to the continuous development of less expensive precursors and more stable sols. On the processing side, more reproducible preparation conditions will be implemented in terms of temperature and humidity control. Concerning coating technologies, it is likely that there will be an increasing use of spray- and roller-coating methods for large area depositions, as well as of ink-jet printing, which has the additional advantage of being applicable to 3-D additive manufacturing. Since the electronics and biomedical applications appear to be the fastest growing segments, one may actually expect increasing examples of 3-D printing of different objects. Bioactive glass scaffolds with tailored porosity for tissue engineering is one outstanding example of such innovative developments (Chapter 8.4).

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8.3

Silica Aerogels

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1 Introduction

As indicated by their name, aerogels are highly porous materials prepared from gels (Chapter 8.2). Even though their solid skeleton can be prepared from inorganic crystalline materials or (bio)polymers with various degrees of crystallinity [1, 2], aerogels made up from amorphous silica are by far the best-studied and also the most relevant industrially, thanks to their outstanding or even record-breaking properties (Table 1). Such features as their unique translucency (Figure 1), high surface area, lowest ambient-pressure thermal conductivity known to man, and low to ultralow density are due to the mesoporous structure (2–50 nm pore diameter) rather than to the amorphous nature of the silica that builds up an open, porous three-dimensional network of linked nanoparticles around the pores. This is why the solid phase in aerogels is not a priori required to be glassy and why other substances can alternatively be used to obtain material properties approaching those of silica aerogels.

When one starts from a condensed gel phase, the basic problem faced to form an aerogel is to eliminate the solvent without causing at the same time a structural collapse of the residual phase through capillary forces. Samuel Kistler solved this problem through supercritical alcohol drying at elevated pressure and temperature when he synthesized the first silica aerogels in the 1930s [3, 4] at the College of the Pacific, California and Stanford University. His work was motivated by basic scientific interest into the structure of gels, but the

resulting aerogels were subsequently produced industrially by Monsanto Chemicals between 1940 and 1960 as thermal insulators and viscosity regulators. Even though the initial discovery of aerogels was made at a university, most of the early development took place in industrial rather than academic settings and much of it is not publicly available. The high citation rate of *silica aerogel* in patent applications, which outnumbers that in the scientific literature between 1930 and 1995 (Figure 2), reflects the importance of these industrial developments.

Together with an industrial revival, academic interest in aerogels took off around 1990. Since then the number of publications has strongly increased and kept track with the number of patents. The renewed interest resulted in major technological breakthroughs (Chapter 8.2) such as the use of alkoxide precursors that circumvent the cumbersome ion exchange needed for waterglass precursors [5]; the advent of supercritical CO₂ drying, which occurs at much lower temperatures compared with supercritical alcohol drying [6, 7]; and the feasibility of ambient-pressure drying which obviates the need for high-pressure equipment altogether [8].

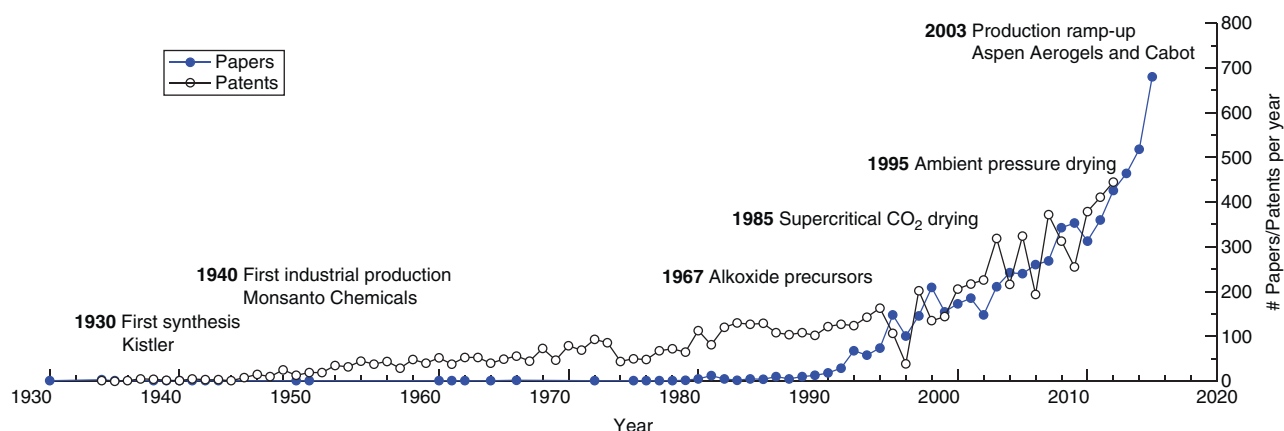
In this chapter, the synthesis and then the particular properties of aerogels will be first described. The manner in which applications rely on these properties will then be presented.

Industrially, these advances have culminated in the production ramp-up of silica aerogel for blankets (Aspen Aerogels) and granulates (Cabot Corporation). As will be also discussed, since then various other manufacturers have entered the market. Finally, attention will be paid to research done in Academia where much of the research focus has been on the characterization of silica-aerogel microstructure and on the development of new metal, metal oxide, polymer, and polymer-silica hybrid aerogels.

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Table 1 Hydrophobic silica aerogel properties.

Composition (wt %)	
• SiO ₂	80–88
• Carbon	10–15
• Hydrogen	2–5
Surface chemistry (molecules/nm ²)	
• Trimethylsilyl groups	2–4
• Silanol/(m)ethoxy groups	0.5–2
Surface area (m ² /g)	500–1000
Primary particle size (nm)	3–5
Secondary particle size (nm)	20–50
Average pore size (nm)	5–60
Density (g/cm ³)	0.08–0.14
Water contact angle (°)	130–160
Sound speed (m/s)	40–1000
Refractive index	1.002–1.050
Thermal conductivity (mW/(m K))	12–18

**Figure 1** Translucency of silica-aerogel granulates where Rayleigh scattering by the solid skeleton results in blue and orange hues for the scattered and transmitted lights, respectively (See electronic version for color figures).**Figure 2** Growing interest in silica aerogels as illustrated first by patents and then by scientific publications that mention this term. Key discoveries highlighted. Source: Data from Google Patents and Web of Science.

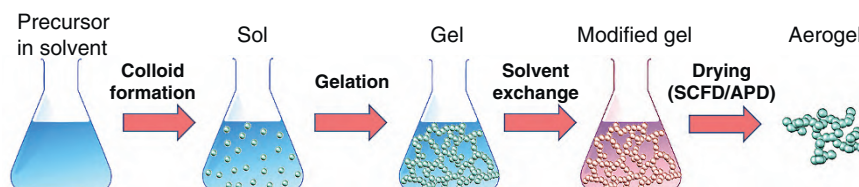
2 Synthesis

2.1 Sol–Gel Chemistry

Silica aerogels are produced through sol–gel synthesis (Chapter 8.2), optional surface modification (hydrophobization), and removal of the solvent (Figure 3). There are two common silica sources, namely, waterglass (Chapter 7.5) and alkoxides (Chapter 8.2). Molecular silicate species and small clusters in ion-exchanged waterglass rapidly aggregate at low pH into silica nanoparticles 2–5 nm in diameter. In academic research, however, the most commonly used precursors are silicon

alkoxides such as tetraethoxysilane [Si(OC₂H₅)₄, TEOS] and tetramethoxysilane [Si(OCH₃)₄, TMOS], which are typically gelled by a two-step acid–base catalyzed sol–gel process [9]. The silica sol is generated from the alkoxides by addition of a solvent (most commonly ethanol or methanol), water, and an acid catalyst. A series of hydrolysis and condensation reactions then takes place, resulting in the formation of SiO₂ nanoparticles along with additional parent alcohol. Regardless of the waterglass or alkoxides silica source, gelation of these slightly acidified sols can be triggered by the addition of a base or additional acid, causing formation of the three-dimensional network of these silica nanoparticles.

Figure 3 Sol–gel synthesis of a surface-modified aerogel.



2.2 Aging and Surface Modification

One can improve the mechanical stability of gels by an aging process whereby, as driven by surface-area minimization, dissolution–reprecipitation reactions akin to Ostwald ripening reinforce the weak interparticle necks. Aging is particularly important for silica gels that will be dried at ambient pressure (i.e. in an oven by simple evaporation) as it enables the gels to withstand the strong capillary forces that occur during the process.

Without a hydrophobization treatment, silica surfaces are covered with silanol groups [$\equiv\text{Si}-\text{OH}$], which makes them inherently hydrophilic: both liquid water and water vapor readily penetrate the aerogel mesopores and cause irreversible shrinkage and pore collapse. Therefore, nearly all commercially available silica aerogels have undergone a surface modification whereby hydrophobic groups, typically trimethylsilyl [$-\text{OSi}(\text{CH}_3)_3$], substitute for hydroxyl or ethoxy groups on the silica surface [10]. This hydrophobization treatment results in water contact angles higher than 140° , prevents water from penetrating into the aerogel's mesopores, strongly limits the humidity uptake, and promotes the so-called spring-back effect during air-pressure drying and under mechanical loading.

2.3 Supercritical Fluid Versus Ambient-Pressure Drying

As already noted, the production of an aerogel inevitably involves a drying step in which the gelation or modification solvent is removed. However, very strong capillary forces act on the aerogel particle network upon evaporative drying because of the small diameters of the pores. They result in condensation reactions between adjacent surface silanol groups that irreversibly cause a strong shrinkage for non-hydrophobized aerogels upon ambient-pressure drying. The resulting materials are relatively dense xerogels with porosities on the order of 50%, rather than the values larger than 90% of aerogels. For the first materials, supercritical alcohol-drying at pressures and temperatures of at least 50–100 bars and 200–400 °C, respectively, had to be used by Kistler to eliminate capillary forces and prevent pore collapse. The advent of supercritical CO_2 drying [6, 7] enabled a drastic reduction in drying temperature down to 40 °C (at 80–100 bar) so that it is now the preferred drying method for most types

of aerogels. Supercritical CO_2 drying is a commercially viable process, but it inevitably involves batch-type processes that require high-pressure autoclaves and add cost and complexity to the production process. Many aerogel-producing companies have therefore adopted the ambient-pressure drying process proposed by Prakash et al. [8], where the hydrophobization of the silica surfaces is followed by conventional, often continuous, evaporative drying. With this methodology, capillary forces are not avoided, but the hydrophobized apolar surface minimizes the interaction between the particles, resulting in a spring-back effect and recovery of up to 95% of the original porosity of a sufficiently aged gel.

3 Properties

3.1 Microstructure and Porosity

Some of the silica-aerogel benefits are due to the glassy nature of the silica particles themselves; for instance, the distinct nanotoxicity advantages compared to materials made from non-biosoluble crystalline silica and silicates [11, 12]. However, most of the unique properties of silica aerogels, and ultimately their applications, critically depend on their microstructure. At the smallest length scales, these aerogels display a “pearl-necklace” structure of silica particles joined together by thin interparticle necks (Figure 4a). The primary silica particles are typically between 3 and 5 nm in diameter and require transmission electron microscopy (TEM) to be observed. They form larger secondary particles typically 20–50 nm in diameter whose ensemble can be more readily observed by scanning electron microscopy (SEM, Figure 4b). The electron-microscopy micrographs clearly point to a highly porous, predominantly mesoporous (2–50 nm) microstructure. Whereas TEM and SEM provide a direct view into the microstructure, statistically more relevant structural information can be obtained from nitrogen sorption (BET), mercury intrusion, and small-angle X-ray and neutron scattering experiments (SAXS and SANS). These measurements confirm the predominantly mesoporous nature of silica aerogels. The scattering experiments, in particular, provide strong evidence for the fractal nature of these materials with typical fractal dimensions around 2.4–2.7 [13]. The small

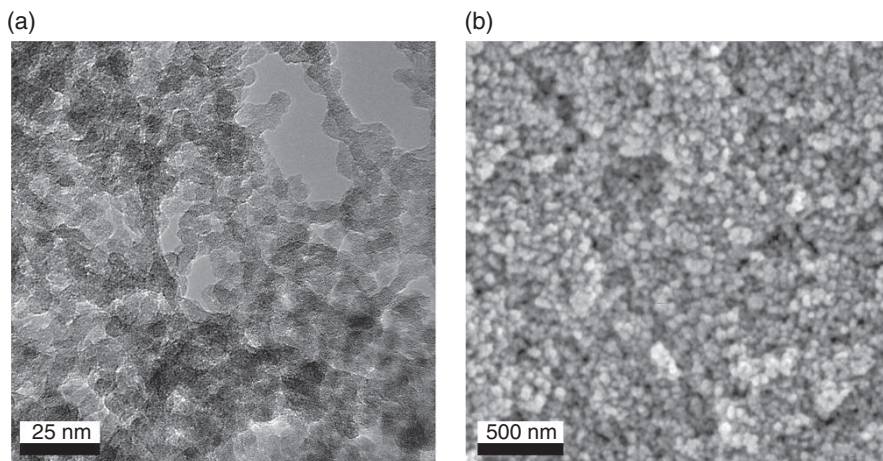


Figure 4 Microstructure of a typical silica aerogel. (a) Pearl-necklace structure highlighted by transmission electron microscopy. (b) Larger secondary particles (20–50 nm) enclosing the mesopores in a scanning electron microscopy micrograph.

diameter of the primary particles leads to large surface areas in the 500–1000 m²/g range.

3.2 Silica and Surface Chemistry

Silica gels prepared without a hydrophobization treatment (and their supercritically dried aerogel analogues) contain a substantial fraction of non-bridging oxygen atoms because of the presence of abundant silanol and/or alkoxide groups ($\equiv\text{Si}-\text{OR}$ where $\text{R}=\text{H}$, CH_3 , C_2H_5). The particle surface thus contains a large fraction of Q^3 species, with minor fractions of Q^2 , in contrast to the particle cores that consist mostly of Q^4 [10], where a Q^n species is a Si atom coordinated by n bridging and $4-n$ non-bridging oxygen atoms (Chapter 2.4). As emphasized above, nearly all commercial silica aerogels have undergone a surface modification treatment to render them hydrophobic and to enable ambient-pressure drying. During hydrophobization, a large fraction of the silanol and (m)ethoxy groups are replaced by trimethylsilyl groups. Depending on the silica precursor and processing steps, the result is a surface coverage with trimethylsilyl, silanol, and (m)ethoxy groups in various proportions. Spectroscopic tools to characterize the surface chemistry are available in the form of Fourier transform infrared (FTIR) (qualitative) and solid-state nuclear magnetic resonance (NMR) spectroscopy (quantitative) (Figure 5). The concentrations and surface coverages of the various functional groups are now well known for a range of archetypal silica-aerogel materials, with typically about three to four trimethylsilyl and one ethoxy/silanol group per nm² of surface area for well-hydrophobized silica aerogels [10].

3.3 Thermal Conductivity

Typical insulation products are highly porous materials in which heat is conducted by means of three major

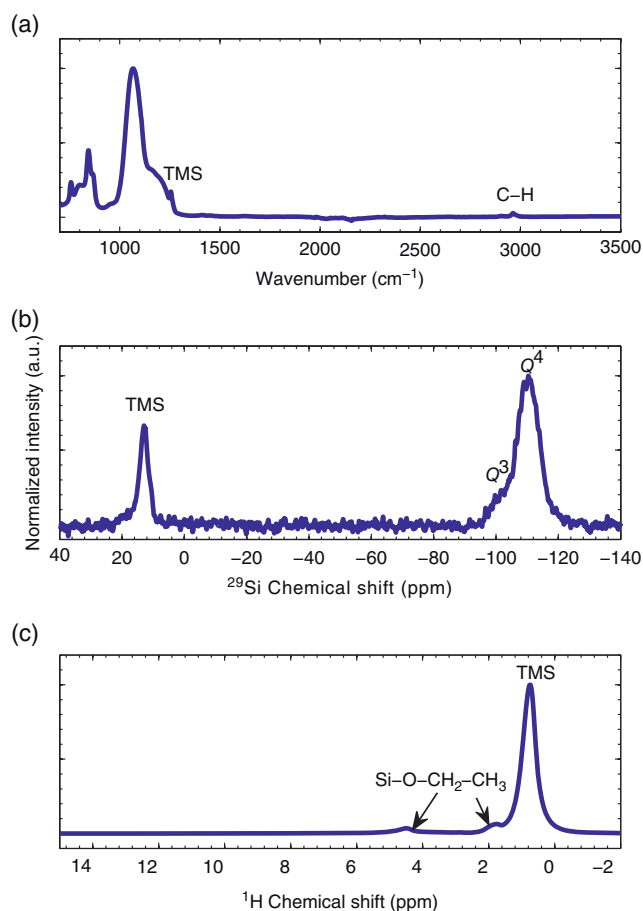


Figure 5 Surface chemistry of a TEOS-based silica aerogel. (a) As probed by Fourier transform infrared spectroscopy. (b and c) By solid-state NMR spectroscopy; peak areas directly giving the relative abundances of the various species.

mechanisms: conduction through the solid skeleton, conduction through the gas inside the pores, and radiation. Of these three, the gas-phase conduction usually dominates. The thermal conductivity of silica aerogels can

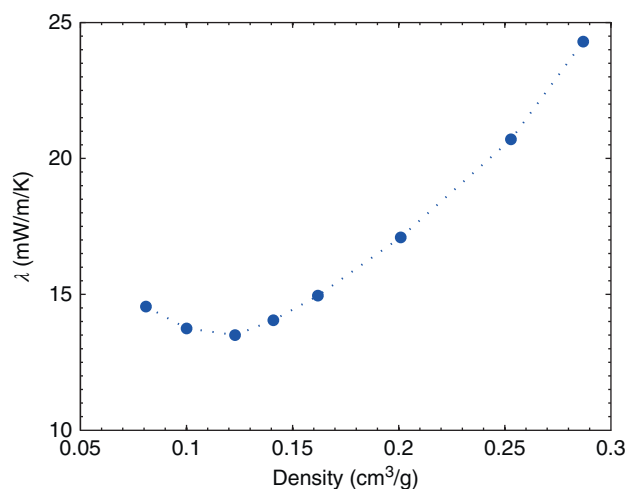


Figure 6 Minimum in the thermal conductivity of aerogels at intermediate densities as illustrated by data for silica aerogels [14].

be as low as 12–18 mW/(m·K) (Figure 6) which is half that of standing air, i.e. 26 mW/(m·K), even though aerogels feature air-filled pores. This low thermal conductivity originates in the mesoporous structure of silica aerogels where most pores are smaller than the mean free path of O_2 and N_2 molecules in air, namely, about 70 nm under ambient conditions. These molecules thus have a higher probability to collide, and thus to transfer kinetic energy, with the pore walls than with other molecules. The heat transfer within the gas phase is reduced, a feature known as the Knudsen effect, and the heat transfer from the pore wall to the gas phase is inherently inefficient.

The solid-phase conduction through the silica particles is also low, thanks to the high porosity of the material, the nanoscopic and thus ultrafine network structure with thin interparticle necks (Figure 4a) and the relatively low thermal conductivity of bulk silica glass of 800–1000 mW/(m·K) at room temperature. Whereas radiative contributions are rather limited at room temperature, infrared opacifiers such as carbon black or titania [TiO_2] are common additives for high-temperature applications for which blackbody radiation would otherwise propagate almost freely through the translucent material.

As commonly observed for insulating materials, aerogels display a minimum in thermal conductivity at intermediate densities (Figure 6), commonly around 0.1 g/cm^3 [1]: at even lower densities, the average pore size approaches the mean free path of air molecules, which causes an increase in gas conduction and radiative transport whereas solid conduction

through the silica skeleton begins to dominate at higher densities [14].

3.4 Mechanical Properties

The often cited high strength-to-weight ratio of silica aerogels is somewhat deceptive as it is more due to low density rather than to outstanding mechanical properties. In fact, the properties of silica aerogels depend very strongly on the density of the material (Figure 7), with brittle behavior for high densities ($\rho > 0.2 \text{ g/cm}^3$), elastic behavior at intermediate densities ($0.2 > \rho > 0.1 \text{ g/cm}^3$), and highly compressible, ductile behavior at low densities ($\rho < 0.1 \text{ g/cm}^3$) [14]. Low-density aerogels can accommodate very large strains but have a Young modulus as low as 0.1 MPa for $\rho \sim 0.050 \text{ g/cm}^3$, whereas high-density aerogels have a high Young modulus of nearly 70 MPa for $\rho \sim 0.350 \text{ g/cm}^3$ but are brittle like glass and fail even at strains lower than 20%.

It should be noted that mechanical data are generally collected under controlled conditions on crack-free laboratory specimens. For real-world applications, the presence of internal cracks and other defects typically results in drastically reduced performance and brittle fracture (Chapter 3.11). As a consequence, silica aerogel applications usually make use of aerogel blankets where individual grains are kept in place by fibers or other products where the aerogel granulate is combined with a binder or placed inside specific cavities. As described in 6, there is thus significant ongoing research on the mechanical reinforcement of silica aerogels at the microscopic structural level such as through addition of various polymers during or after gelation.

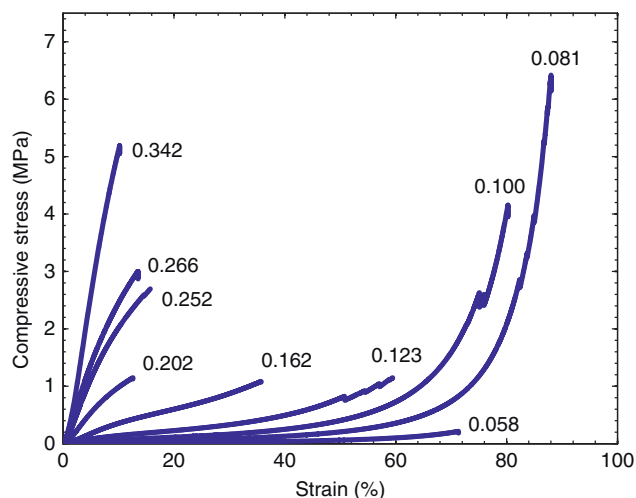


Figure 7 Density-dependent uniaxial compression curves for silica aerogels [14].

4 Applications

4.1 Thermal Insulation

By far the best-established application of silica aerogels is as thermal superinsulators [15, 16]. The unique selling point of silica aerogel is an ultralow thermal conductivity, but additional advantages are a relatively low flammability, a vapor open structure, and hydrophobicity. The low thermal conductivity enables one to use thinner insulation to reach the same thermal performance as with conventional materials. This advantage is offset by the high cost of silica aerogel products, which is up to 20 times higher than that of mineral wool. As a result, most applications are in niche markets where either space for thicker insulation is not available or where space savings result in large cost savings.

The former case is that of the building sector for which aerogels have given rise to a wide range of technical solutions: boards, translucent elements, blankets, or renders and concrete (Figure 8). These are particularly valuable for building retrofit where the use of thick layers of conventional insulation materials is often impossible for technical or aesthetical reasons, in particular in buildings under heritage protection. Likewise, silica-aerogel insulation is beginning to find its way into new buildings, particularly in areas with high property prices (e.g. inner city centers) where the gain in usable floor space offsets the added cost of an aerogel solution. In addition, these products are often used to eliminate thermal bridges at specific locations in a façade.

Currently, however, the largest silica-aerogel market is industrial insulation. Blankets are particularly common materials for pipe insulation (Figure 8e), including oil-and-gas pipelines for which space savings translate into very large cost savings during transport and installation. In addition, silica aerogel is mechanically and chemically stable up to at least 300 °C and the permanent hydrophobic nature of such products eliminates liquid (sea)water intrusion and thus positively affects the corrosion resistance of steel pipe assemblies.

4.2 Alternative Applications

The unique properties of silica aerogels have also given rise to non-insulating applications, albeit at much smaller production volumes. Of note are space applications, which have driven substantial research and development on both silica- and polymer-based aerogels where NASA has been a key player. A low-density silica aerogel has, for instance, been used as a capture material for hypervelocity cosmic dust particles because its mesostructure ensures a sufficiently gentle dissipation of the particles' kinetic energy and allows their intact capture, whereas

its transparency enables an easy recovery of the impacted particles for the variety of chemical and physical analyses performed to understand better cosmochemical processes (Figure 8d) [17]. Other applications are based on silica aerogels' low refractive index for the detection of Čerenkov radiation [18] or exploit their large surface area and/or sorption capacity: additives for foundry applications [19], oil-spill clean-up materials [20], catalyst support materials [21], gas adsorption [22], and drug delivery [23].

5 Markets and Industrial Production

5.1 Markets

A recent Markets and Markets study estimates the 2014 global aerogel market at 200–300 MM US\$ with a compound annual growth rate of 19%, leading to a predicted 2019 aerogel market of over 500 MM US\$ [24]. Aspen Aerogels, the market leader in silica-aerogel products, fabricates a variety of hydrophobic, fiber-reinforced silica-aerogel blankets and reported a marked increase in its revenues of 63 (2012), 86 (2013), 102 (2014), and 122 (2015) M US\$, corresponding to an estimated ramp-up in production volumes from 20 000 to 50 000 m³ over this period. These numbers are in line with several existing market research studies, particularly with respect to the compound annual growth rates. Cabot Corporation, a global chemicals and materials manufacturer, probably is the second largest aerogel producer with a turnover of ~20 MM US\$ from a production of 5 000–10 000 m³ of silica-aerogel granulate per year. In addition to these well-established players, a great many new companies have recently entered the market, including Enersens, Guangdong Alison, and Nano High-Tech Co., which all produce a variety of silica-aerogel products (granulate, powders, boards, and blankets) and also JIOS Aerogel, which specializes in silica-aerogel powders. Even though the oil-and-gas segment accounts for about 75% of the current market, the fastest growth rates are expected from the construction and automotive/transportation sectors [24].

5.2 Production Technology

Two types of precursors (waterglass and alkoxides) and two drying technologies (supercritical CO₂ and ambient-pressure) are applied industrially for silica-aerogel production. Aspen Aerogels and most likely Guangdong Alison and Nano High-Tech Co. as well use silicon alkoxide precursors as the silica source and supercritical CO₂ drying to remove the pore fluid. In contrast, Cabot Corporation and JIOS Aerogel use waterglass

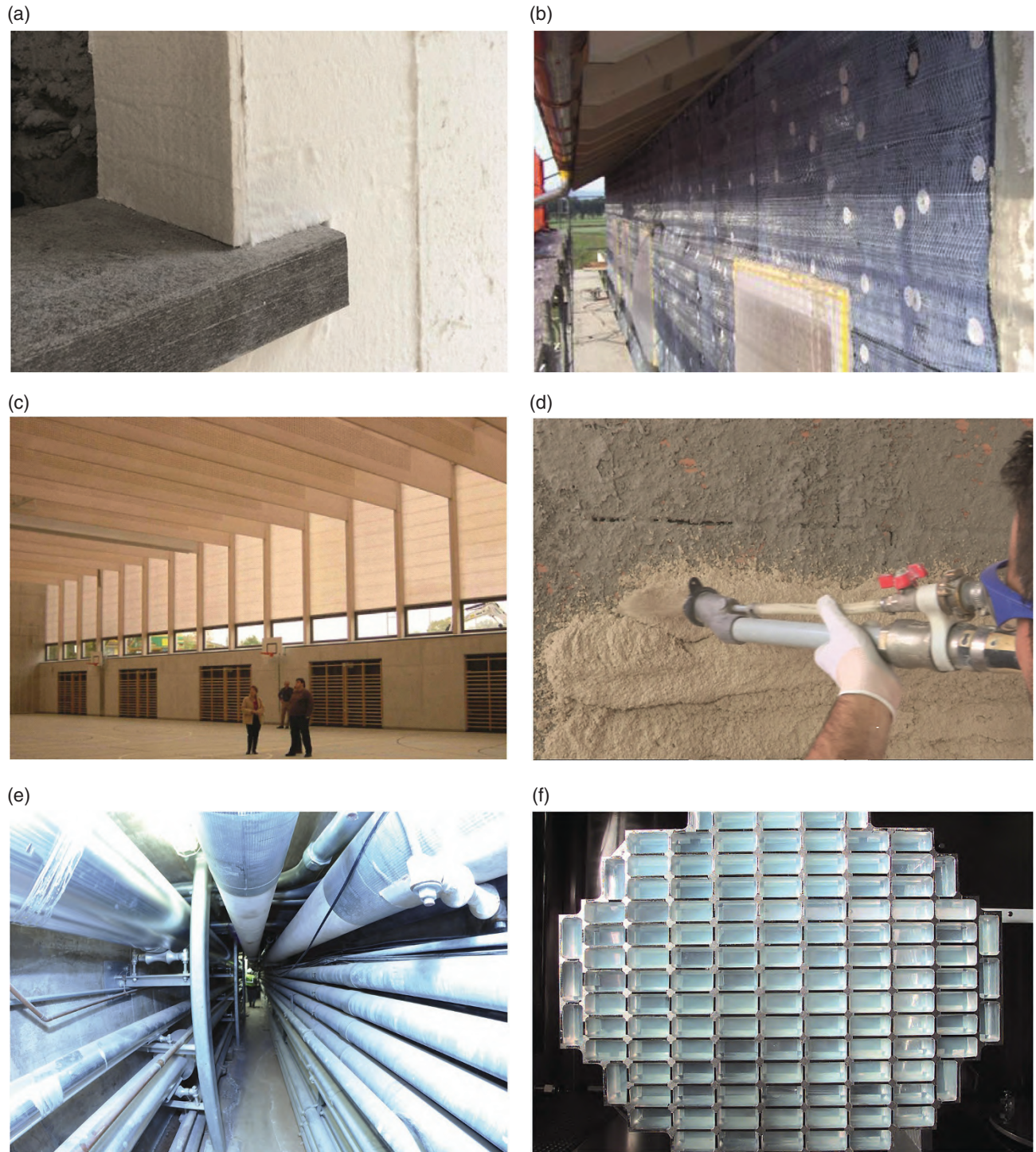


Figure 8 Some applications of silica aerogels. (a) Building retrofit with Heck Aero boards (*Source: AGITEC AG*). (b) Building retrofit with Spaceloft aerogel blankets (*Source: Max Schweizer AG*). (c) Translucent elements for building insulation. (d) Render for building retrofit applications (*Source: Fixit AG*); (e) Blankets for pipe insulation (*Source: Aspen Aerogels*). (f) Blocks of the tennis racket sized Stardust dust collector (*Source: JPL/NASA*).

precursors and ambient-pressure drying for their respective granulate and powder production. Enersens combines alkoxide precursors with ambient-pressure drying. This variety of production technologies, combined with the high contributions of processing and overhead to the total production cost (compared to the starting materials), indicates that silica aerogel production has not reached full industrial maturity. This is in sharp contrast to established industries such as float glass (Chapter 1.4) or glass and mineral wool (Chapter 9.3) production.

6 Silica Hybrid Aerogels, Aerogel Composites, and Non-silica Aerogels

Common silica aerogels are rather brittle and their products can be quite dusty. As a result, significant academic and industrial research and development is devoted to the development of alternative aerogels with improved mechanical properties. Silica-like aerogels from methyltrimethoxysilane [$C_4H_{12}O_3Si$] precursors are highly flexible [25], but often display reduced surface areas and higher thermal conductivities. Bulk polymers and biopolymers are less brittle than inorganic glasses, which is also reflected in the corresponding aerogels. However, polymer and biopolymer aerogels typically suffer from a higher thermal conductivity and flammability. Therefore, much of the ongoing research on (bio)polymer aerogels aims at improving these properties [26]. An alternative approach aims at reinforcing silica aerogels through hybridization with various (bio)polymers [27, 28].

Most often, however, improvements in mechanical properties come at the cost of an increase in thermal conductivity. Some of these materials are nonetheless of industrial interest, thanks to a combination of a high strength-to-weight ratio with a moderately low thermal conductivity. Recently, an increase of the mechanical strength and a decreased dust release has been achieved through the addition of the biopolymer pectin prior to gelation, without a significant increase in thermal conductivity [29]. Alternatively, silica aerogels can be combined with stronger materials to build composites, for example, as aerogel embedded concrete [30] or by casting silica aerogel into honeycombs [31]. Although relatively far from the market, aerogels with unique properties have been prepared from a wide variety of materials such as metals, carbons, carbon nanotubes, graphene, titanium oxide, zirconia, etc., for battery, sorption cooling, solid oxide fuel cell, and catalysis applications [2].

7 Perspectives

The unique properties of silica aerogels, in particular their ultralow thermal conductivities, make them very attractive materials for a range of applications. Silica aerogels already constitute a rapidly growing niche market today, but a drastic reduction in production cost is required to enable them to penetrate the main insulation markets. Although suffering also from the price of the starting materials, the current high production costs are mostly related to the capital and operational expenses of a complex production process that involves lengthy and resource-intensive batch-type solvent exchanges (Figure 3) and, in the case of supercritical drying, expensive high-pressure equipment. However, continuous drying processes are under development and progress is also achieved toward a minimal solvent production process that would speed up the production process and limit the solvent consumption (1.2 m^3 of solvent for 1 m^3 of aerogel) to nearly the theoretical minimum of 1 m^2 of solvent for 1 m^3 of aerogel [32]. Such technological improvements, continuing innovation by the current market leaders, and the entry of new producers are signs of an overall maturation of the market that is expected to lead to a cost reduction of silica aerogels. This market maturation will lead to an expansion of the aerogel market beyond its current niches and with growth rates still higher than the current ones.

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8.4

Bioactive Glasses

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1 Introduction

Glass is used in a wide variety of medical and dental applications, including chemically strengthened glass for epinephrine (adrenaline) autoinjectors (EpiPen®), silver-releasing glass for urinary catheters, glass fillers in dental composites, or glass-ceramic dental crowns. Bioactive glasses, by contrast, are designed to actively interact with the human body, release ions, and degrade over time [1].

Bone defects arising from disease (e.g. osteoporosis or tumor removal), trauma, or congenital defects, which are too large for the bone to heal itself, are usually treated with either allografts (i.e. donor bone) or autografts, which involve transplanting bone from another part, usually the pelvis, of the patient's body to the site of the defect. Both methods have disadvantages, however, among them being limited supply of bone and side effects such as pain at the donor site. Allografts, in addition, require careful screening to avoid the risk of transmitting diseases. Synthetic alternatives such as bioactive glasses can overcome these issues [2].

Bioactive glasses were developed by Larry Hench in the late 1960s [3], following a chance conversation with a colonel of the US army, who challenged him to produce a material that would not be rejected by the human body [4]. Knowing many soldiers who, following severe injuries during the Vietnam War, had their limbs amputated, the colonel realized that one reason was that the implant materials available at the time (bioinert metal and polymers) did not bond to body tissue but were rejected instead. Hench thus decided to experiment with a SiO₂-poor soda-lime silicate composition to which

P₂O₅ was added. His Bioglass 45S5, a phosphosilicate glass of the composition 46.1 SiO₂•2.6 P₂O₅•26.9 CaO•24.4 Na₂O (in mol %), turned out to be the first synthetic material to form an intimate bond with bone [5]. Before this discovery, implant materials were designed to be chemically inert to avoid any foreign body reaction in the human body. Bioactive glasses, by contrast, degrade in physiological solution, release ions, and form a surface layer of apatite. It is this combination of dissolution and apatite mineralization that makes bioactive glasses so successful at regenerating bone: bioactive glass granules implanted into a bone defect act as a three-dimensional (3-D) template to guide bone growth and help the bone to heal while they degrade.

Since the invention of the original bioactive glass, more compositions have been developed, many of them at Åbo Akademi in Turku, Finland. Among these are glasses S53P4 [6] and 13-93 [7], the latter being the first bioactive glass that could be processed at high temperatures without crystallizing. Further selected compositions are presented in Table 1. Two bioactive glasses, Bioglass 45S5 and S53P4 (BonAlive®), have approval by the US Food and Drug Administration (FDA) for a range of clinical applications [8]. They have now been used in more than a million patients and are gathering popularity among orthopedic surgeons.

In this chapter, we will describe two approaches for preparing bioactive glasses, namely, the high-temperature melt route and the sol-gel process. We will also look into their mechanism of interaction with body fluids before looking at current and possible future applications.

2 Melt-Derived Bioactive Glasses

Melt-derived bioactive phosphosilicate glasses consist of a silicate network of connected SiO₄ tetrahedra

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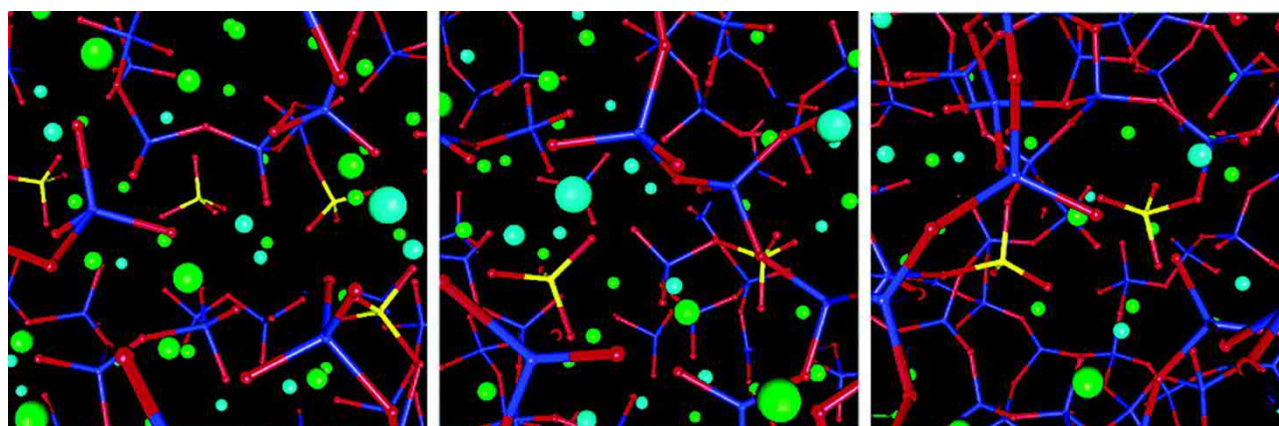
L. Hupa, Process Chemistry Centre, Åbo Akademi University, Åbo, Finland

Encyclopedia of Glass Science, Technology, History, and Culture, Volume II, First Edition. Pascal Richet.

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Table 1 Selected bioactive glass compositions (mol %), network connectivity of the silicate network (NC_{Si} ; corresponding to the average number of bridging oxygen atoms, BO, per silicon atom), and the average number of nonbridging oxygen atoms (NBO) per silicon atom.

Glass	SiO ₂	P ₂ O ₅	B ₂ O ₃	Na ₂ O	CaO	CaF ₂	K ₂ O	MgO	NC_{Si} (BO/Si)	NBO/Si
45S5	46.1	2.6	—	24.4	26.9	—	—	—	2.1	1.9
S53P4	53.9	1.7	—	22.7	21.8	—	—	—	2.5	1.5
13-93	54.6	1.7	—	6	22.1	—	7.9	7.7	2.6	1.4
ICIE16	49.5	1.1	—	6.6	36.3	—	6.6	—	2.1	1.9
ICIE1-F1	49.0	1.1	—	26.1	22.8	1.0	—	—	2.1	1.9
0106	51.4	1.7	0.2	5.9	24.9	—	7.9	8.1	2.4	1.6
1106	61.2	0.5	—	5.1	23.2	—	10.0	—	2.8	1.2

**Figure 1** Decreasing concentrations of modifier ions (spheres) and increasingly cross-linked silicate network (ball-and-stick models) for increasing silica contents as obtained from molecular dynamics simulations: Bioglass 45S5 (left) and glasses with 55 (center) and 65 mol % SiO₂ (right). Source: Reproduced from [9] with permission from the American Chemical Society.

(Chapter 2.1); however, in contrast to more chemically stable silicate glasses, bioactive glasses contain larger concentrations of modifier oxides, resulting in the presence of large numbers of nonbridging oxygens (Figure 1) and a lower network connectivity (a smaller average number of bridging oxygens per silicon atom; Table 1) [10]. Generally, bioactive glasses have a network connectivity between 2 and 2.6.

In addition, many bioactive silicate glasses contain small amounts of phosphate, usually up to 6 mol % P₂O₅. Although it was originally thought that SiO₂ and P₂O₅ form a mixed network containing Si—O—P bonds, it has now been recognized by solid-state ³¹P NMR results that most of the phosphorus is present as orthophosphate (PO₄³⁻) tetrahedra, charge-balanced by modifier cations [10]. Besides NMR spectroscopy and MD simulation, results have also shown the presence of phosphate clusters in these glasses, which might indicate the presence of phase separation.

The structural characteristics of bioactive glasses, i.e. their highly disrupted silicate network and the presence

of orthophosphate groups, are key to properties such as the ability to degrade, release ions, and form the biomimetic apatite surface layer described below. Unfortunately, they also cause bioactive glasses to have a pronounced tendency to crystallize when processed at higher temperatures, e.g. during the sintering of glass powders to make scaffolds or the drawing of fibers from the melt.

The crystallization tendency varies with glass composition, because more cross-linked silicate networks and lower concentrations of alkali ions (and higher concentrations of divalent ions) reduce it and improve glass processing. In many bioactive phosphosilicate glasses, crystalline silicate phases such as wollastonite (CaSiO₃) or sodium calcium silicates form during heat treatment [11]. Glasses with higher phosphate contents, by contrast, precipitate phosphate-containing crystal phases, including fluorapatite in fluoride-containing glasses [12]. In order to reduce the crystallization tendency of bioactive glasses and improve their processing, intermediate oxides such as magnesium oxide have been incorporated. The

combination of sodium and potassium oxide also improves processing by making use of the mixed alkali effect (Chapter 4.6).

The pronounced crystallization tendency of bioactive glasses such as Bioglass 45S5 is the reason why bioactive glass is available commercially in the form of granules (“morsels”) mostly rather than porous scaffolds and why the sol–gel route was investigated for the preparation of scaffolds as described in the following section. In recent years, however, new bioactive glasses, which are optimized for high-temperature processing without crystallization occurring (e.g. 13-93 or ICIE16; Table 1), have been developed and are being investigated for the preparation of scaffolds.

3 Bioactive Sol–Gel Glasses

The sol–gel process involves the room-temperature assembly of silica nanoparticles forming from the hydrolysis of alkoxide precursors, such as tetraethylorthosilicate (TEOS), the most popular precursor for silicate-based sol–gel glasses (Chapter 8.2). Under acidic catalysis, the nanoparticles agglomerate, polycondensation occurs through formation of —Si—O—Si— bonds, and the nanoparticles fuse together. When the condensation by-products are evaporated through drying, nanopores are left in the interstices between the nanoparticles. These nanopores are in the mesoporous (2–50 nm) range and are interconnected but random in their distribution.

Owing to the nature of the sol–gel process, the silicate network contains many Si—OH groups, which are a result of the polycondensation in a water-based sol. The protons (H^+ ions) act as network modifiers as do Na^+ ions in a melt-derived glass. This means that it is difficult to predict the network connectivity of the silicate network of a sol–gel glass from the nominal composition. After gelation the gel will contain a certain amount of H^+ , and, as drying and stabilization occurs, more Si—O—Si bonds form, increasing the connectivity. This transformation has an impact on degradation rate and bioactivity (see later).

In bioactive sol–gel glasses, phosphates are introduced as phosphate alkoxides (e.g. triethylphosphate [TEP]), whereas calcium is added to the sol as a salt, most commonly calcium nitrate. The phosphate plays a similar role here as it does in the melt-quenched glass structure, forming orthophosphate (PO_4^{3-}) groups. This is partly because TEP already has an orthophosphate-like structure before it is hydrolyzed [13]. Calcium incorporation is more challenging. When calcium nitrate was first used, the assumption was that when it dissolves in the sol, calcium will disrupt the formation of the silicate network,

taking its role as a network modifier. Actually, a silicate network forms at room temperature during the gelation stage, and the calcium only enters the network if the gel is heated above 450°C [14]. This has implications for the low-temperature synthesis of bioactive compositions, particularly for the preparation of hybrid materials combining organic and inorganic phases, as described in Section 8. Calcium alkoxides, e.g. calcium methoxyethoxide [15], can be selected in place of calcium nitrate, but their reaction rates are difficult to control so that their use is in its infancy [1, 8].

A benefit of the bottom-up sol–gel approach is that one can prepare porous scaffolds without having to sinter the glass (Figure 2) as a foaming step can be introduced prior to gelation. This foaming is achieved by vigorous agitation with the aid of a surfactant and hydrofluoric acid (HF) acting as a catalyst through formation of complexes with the silicate network, which increases the rate of gelation. This step is critical as the viscosity of the sol must increase rapidly to support the pores that form around the surfactant [1]. The surfactant in the sol–gel foaming process acts as a template for the formation of macropores, which are in excess of $500\ \mu\text{m}$. The surfactant is later removed by thermal processing.

An exciting potential application of sol–gel technology in biomedical research is the use of mesoporous silica nanoparticles in therapeutic applications. In these particles, the mesopores are in ordered arrays because surfactants have been used as templates. In this case, however, the surfactant molecules form micelles and pack as spheres into regular crystal-like arrays. When the surfactant is burned out, ordered arrays of interconnected mesopores remain. They are most useful in the form of nanoparticles, e.g. in the 50–150 nm range. Monodispersed nanoparticles can be synthesized through modification of the Stöber process. This process uses TEOS in water but employs a catalyst of high pH such as ammonium hydroxide, which not only promotes polycondensation but also causes the sol nanoparticles to repel each other, creating spherical nanoparticles.

These mesopores are useful because they can enhance the degradation rate of the silica (dense Stöber silica particles are nondegradable) and they can be used to carry drugs. An approach is to load the mesopores with a chemotherapy drug by diffusion in an appropriate medium. The hypothesis is that the particles can be injected into a tumor, or near it, and the tiny particles will pass through leaky blood vessel walls in the tumor, arriving at cancer cells. As the particles are small (e.g. 80 nm), they will enter the cells. The chemotherapy drug will diffuse out of the mesopores gradually, providing a sustained dose to the local area, which would be an advantage compared over biodegradable polymer capsules, which tend to release the drugs in a sudden burst. The challenge for the silica

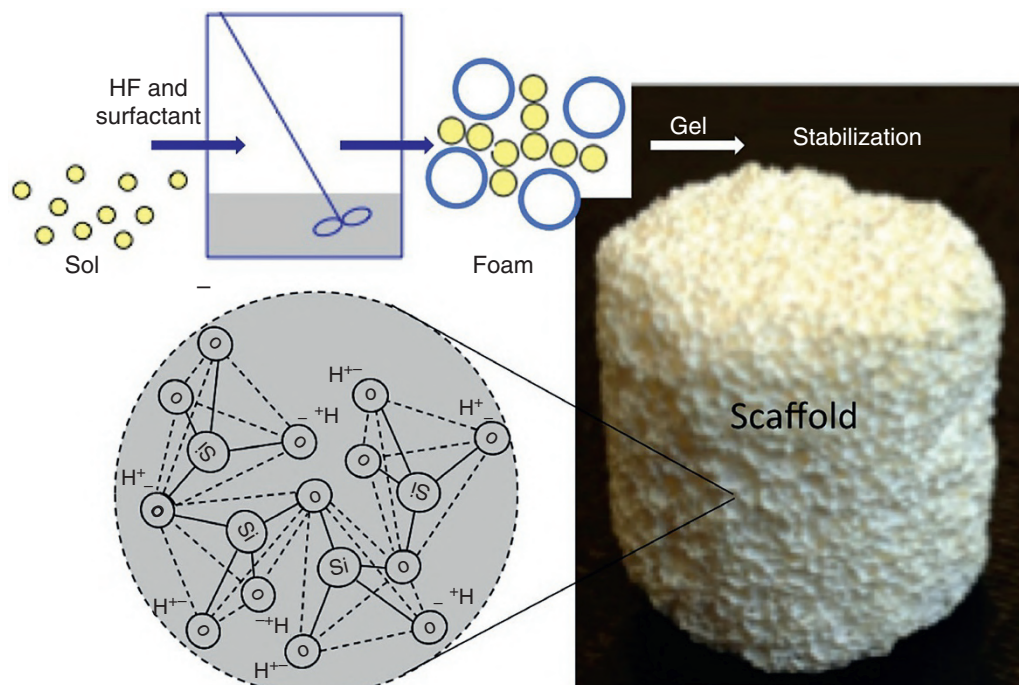


Figure 2 Schematic of the sol-gel process and foaming step that can be introduced to produce highly porous scaffolds for bone regeneration.

particles is that the drug can leach out of the mesopores before the particle reaches the cancer cell. A recent study [16] reported the concept of a protocell that has mesoporous silica at its core, which contains the drug and quantum dots (Chapter 6.6) that will allow tracking of the device. Around the core is a polyethylene-glycol jacket that shields the particle from macrophage cells, which try to engulf it and remove it from circulation. Attached to the jacket are molecules that can target receptors specific to cancer cells and trigger the opening of the vesicles inside the intended targeted cells.

Bioactive versions of mesoporous particles are being investigated, but a challenge here is to get a high cation (e.g. calcium) content when salt precursors are used [17].

4 Degradation and Apatite Formation

When in contact with aqueous solutions (including body fluids *in vivo* as well as simulated physiological solutions such as simulated body fluid [SBF] or cell culture solutions during *in vitro* studies), water molecules can easily enter the silicate network. This is made possible owing to its highly disrupted structure with large numbers of non-bridging oxygens (large NBO/Si ratio; Table 1). This leads to rapid ion exchange whereby modifier cations are released into the surrounding medium and replaced by

protons from the solution, resulting in the formation of silanol (Si—OH) groups. Formation of this ion-depleted silicate (or silica gel) layer can be observed by Fourier transform infrared spectroscopy measurements. A main difference compared to more chemically stable silicate glasses is that in bioactive glasses this ion exchange process does not happen near the surface only, but results in ion release from deeper within the bulk of the glass. This difference has been highlighted in dynamic dissolution experiments in 2-amino-2-hydroxymethyl-propane-1,3-diol (Tris) buffer, which showed different release profiles (Figure 3) depending on whether the glass possessed high, intermediate, low, or no bioactivity [18]. Other factors, such as modifier-ion field strength, are also important and have a strong influence on solubility, with larger field strengths resulting in slower degradation.

When in contact with fluids, ions released from bioactive glasses – particularly calcium and phosphate – cause local supersaturation and subsequent precipitation of a surface layer of apatite (usually described as hydroxycarbonate apatite) (Figure 5). This layer is similar to the apatite found in mineralized human tissue including bone, dentine, and enamel, as it is nanocrystalline and shows various substitutions (e.g. with carbonate) in the crystal lattice. It has thus been described as biomimetic.

As a highly disrupted silicate network with a high concentrations of modifier cations facilitates water intrusion and ion exchange, variations in silicate network

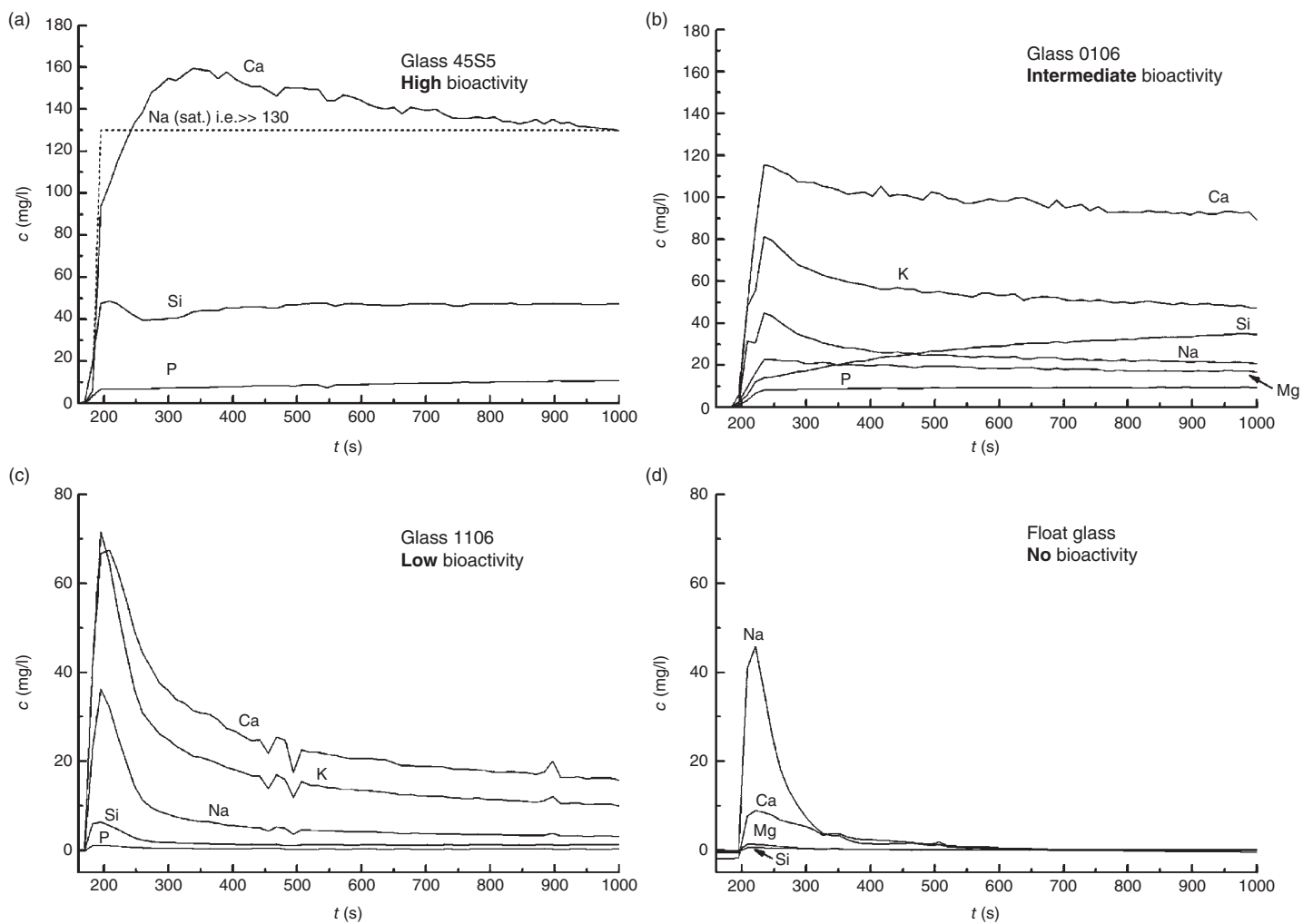


Figure 3 Four typical initial ion release profiles for dynamic dissolution experiments of glasses: (a) 45S5, (b) 0106, (c) 1106, and (d) float glass in Tris buffer solution. Source: Reproduced from [18] with permission from Elsevier.

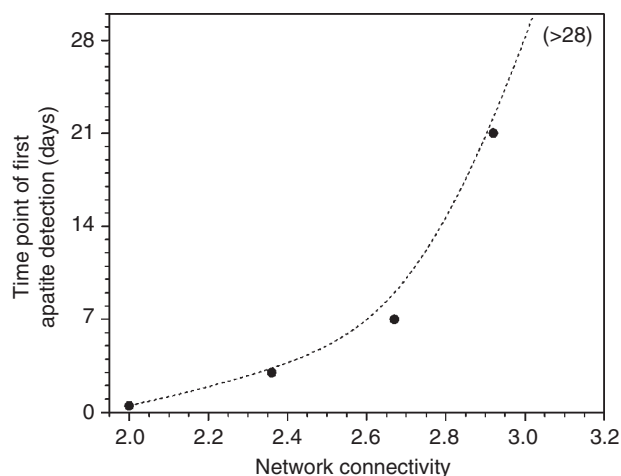


Figure 4 Time point of first apatite formation for $\text{Na}_2\text{O-CaO-SiO}_2$ silicate glasses immersed in simulated body fluid (as detected with thin-film X-ray diffractometry and Fourier transform infrared reflection spectroscopy) vs. network connectivity of the silicate network. Calculated and plotted based on data from [19].

polymerization and network connectivity result in slower or faster degradation and apatite formation (Figure 4). For glasses with increasing network connectivity, apatite formation is significantly delayed and, ultimately, not observed at all [19].

The rate of apatite formation is strongly affected by various other factors such as the presence of other ions (strontium or fluoride), presence of silanol groups (acting as nucleation sites), and a local pH rise (caused by the proton depletion of the aqueous medium as a result of exchange with modifier ions). Some bioactive glass components, such as magnesium or zinc, negatively affect apatite precipitation, as they are thought to inhibit apatite nucleation.

The *in vivo* degradation of bioactive glass is controlled by dissolution rather than by cellular or enzyme action [1]. The presence of silicon-containing species in urine has been observed in animal studies, suggesting that the dissolution products from bioactive glasses are excreted rather than accumulated in the body. This conclusion has been confirmed by clinical studies, which showed no elevated silicon concentrations in the blood of adults or children bearing bioactive glass implants.

Sol-gel glasses tend to undergo dissolution more rapidly than their melt-derived counterparts for two reasons. The first is that they have an enhanced specific surface area owing to their inherent nanoporosity. The second reason is that the sol-gel process leaves protons in the glass structure, acting as additional network modifiers, forming Si-OH groups, and reducing the network connectivity. These Si-OH groups on the glass surface

provide many sites for apatite nucleation. An additional benefit is that cells attach more readily to a nanotextured surface than to smooth surfaces. Melt-derived glasses, by contrast, tend to possess a nanorough surface after apatite formation only.

5 Biological Response

Bioglass® 45S5 positively affects the cell cycle, resulting in faster turnover of osteoblast (bone-forming) cells and, as a consequence, in a more mature cell population capable of producing mineralized tissue within a relatively short time [20]. Experiments using the dissolution products of 45S5 showed that osteoblast proliferation is increased via gene upregulation caused by ions released from the glass. This feature is particularly interesting for tissue engineering applications, as it suggests that supplementation with growth factors is not needed for bioactive glasses, unlike for other bioceramics such as calcium phosphates.

In vitro cell tests have shown an influence of the glass network connectivity on cell proliferation. More polymerized glasses show lower cell proliferation than less polymerized ones, in agreement with predictions based on *in vitro* immersion tests [21]. This effect can be explained by a range of factors such as slower apatite formation (reducing protein adsorption and initial cell attachment; Figure 5) and reduced ion release (in particular for calcium ions and silica species, which stimulate osteoblast proliferation and differentiation) for more polymerized glasses.

In vivo studies in rabbits have shown that Bioglass 45S5 particles lead to faster bone formation than synthetic hydroxyapatite particles and, unlike apatite, also completely degrade over time [22]. These results allow for bone regeneration, whereas glass particle dissolution correlates with bone formation. Further animal experiments in rabbits showed that bone formation is significantly reduced *in vivo* for glasses with increasing network connectivity (Figure 6). This confirmed the results from *in vitro* immersion tests showing much slower apatite formation with increasing network connectivity (Figure 4). Glasses with low network connectivity degraded *in vivo*, whereas those with a high network connectivity did not show signs of degradation but showed fibrous tissue encapsulation instead.

Vascularization is a critical step during tissue regeneration, as cell proliferation depends on the supply of oxygen and nutrients. Bioglass 45S5 has been suggested to enhance angiogenesis, i.e. the formation of new blood vessels *in vivo* [23].

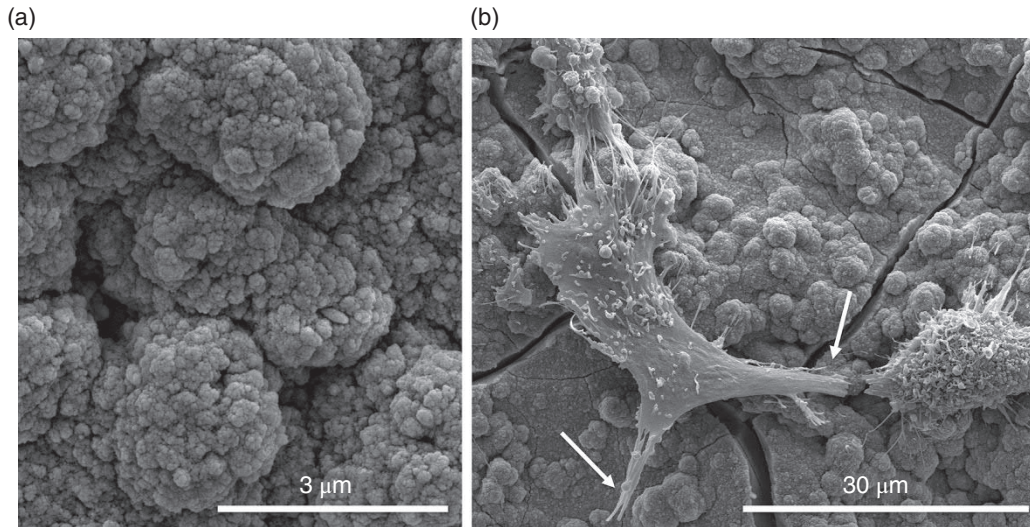


Figure 5 (a) Apatite surface layer formed on the fluoride-containing bioactive glass ICIE1-F1 (Table 1) during immersion in RPMI 1640 cell culture medium supplemented with 10% fetal bovine serum for seven days and (b) human osteosarcoma cell at 14 days attached onto the same glass composition, showing a flattened morphology and being anchored to the substrate by several lamellipodia (arrows).

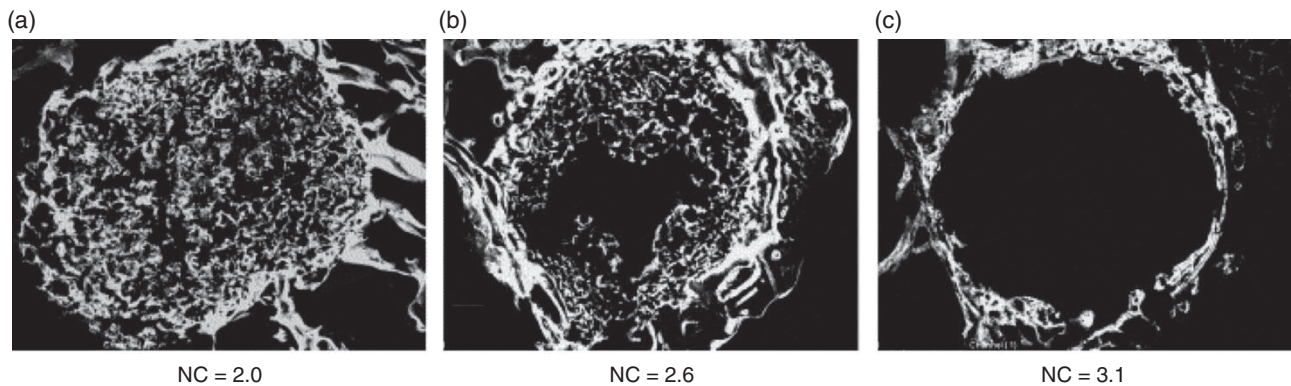


Figure 6 (a) Histomorphological results showing calcein fluorescence-labeled new bone formed on $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ glasses at six weeks after implantation. Network connectivity was (a) 2.0, (b) 2.6, and (c) 3.1. Diameter of the circular area is 6 mm. Source: Reproduced from [19] with permission from Pergamon.

6 Therapeutic Ions in Bioactive Glasses

One of the fundamental advantages of glasses is the possibility of varying their composition without many of the stoichiometric restraints imposed on crystals. It is therefore possible to incorporate cations, which have physiological activity and therapeutic properties, at varying concentrations. This would allow these ions to be released during the dissolution process. Particularly those ions acting as modifiers in the glass are released readily in exchange for protons from the surrounding aqueous medium (Chapter 5.11). Once released, these ions can

perform their therapeutic action [24], as demonstrated during *in vitro* experiments.

Calcium ions constitute one of the main components in many bioactive glasses and are readily released upon contact between glass and water. They favor not only apatite formation but also osteoblast differentiation. Strontium-substituted bioactive glasses stimulate the bone-forming cells (osteoblasts) while preventing osteoclasts from resorbing bone, as do strontium-containing drugs for treating osteoporosis [25]. This makes them particularly interesting implant materials for patients suffering from osteoporosis, as they could enhance bone regeneration without needing additional medication.

Cobalt-containing bioactive glasses enhanced angiogenesis *in vitro* by mimicking hypoxia, i.e. low oxygen pressure conditions.

Silver ions have long been known to exhibit antibacterial properties. Owing to a similar charge to size ratio as sodium ions, they can be incorporated into glasses by molten-salt ion exchange. The similarity between Ag^+ and Na^+ results in a similarly fast release of silver ions, allowing for antibacterial action. Zinc-containing bioactive glasses have been developed, as zinc ions are not only known to be bactericidal but also essential for wound healing. Appropriate release levels of zinc ions have to be maintained, however, as too high concentrations of zinc are cytotoxic.

Fluoride-containing bioactive glasses are of interest for dental applications to prevent dental caries, as fluoride-releasing bioactive glasses form fluorapatite in physiological solutions, which is more stable against acid attack than hydroxycarbonate apatite.

7 Applications of Bioglasses

Most commercial bioactive glass products (such as Peri-oGlas®, NovaBone®, NovaMin®, BonAlive, Biogran®, or Sylc®) are phosphosilicate glasses [26]. Other glasses used as biomaterials (e.g. phosphate or borate glasses) will only be mentioned briefly here.

7.1 Orthopedics

Bioglass 45S5 was originally developed as a bone-replacement material. Its first use was as middle-ear prostheses or for orbital-floor reconstruction [1]. In these early applications, monolithic devices were used, either custom-made for each individual patient or of standard (such as conical) shape. After animal studies had shown that bioactive glasses degrade while stimulating formation of new bone [27], interest grew in their use to regenerate bone. Implant studies in alveolar sockets showed that bioactive glass particles degrade over time, resorption rates being significantly faster than for demineralized freeze-dried bone allograft. The ability of Bioglass 45S5 to promote angiogenesis is of great advantage here, as bioactive glass implants can enhance vascularization and therefore accelerate bone regeneration.

Long-term studies on bioactive glass BonAlive S53P4 (Figure 7) have shown that the glass is well tolerated in children and adults, allowing for bone remodeling, vascularization, and cartilage repair. Depending on the size of the defect and nature or size of the glass granules used, the bioactive glass implant disappears gradually over periods of one to four years by a combination of surface reaction, dissolution processes, and possibly also resorption activity of osteoclast cells [29].

Bioactive glasses are particularly suitable for treating fractures and defects in cancellous (spongy) bone. Clinical results suggest that bioactive glass works as well as

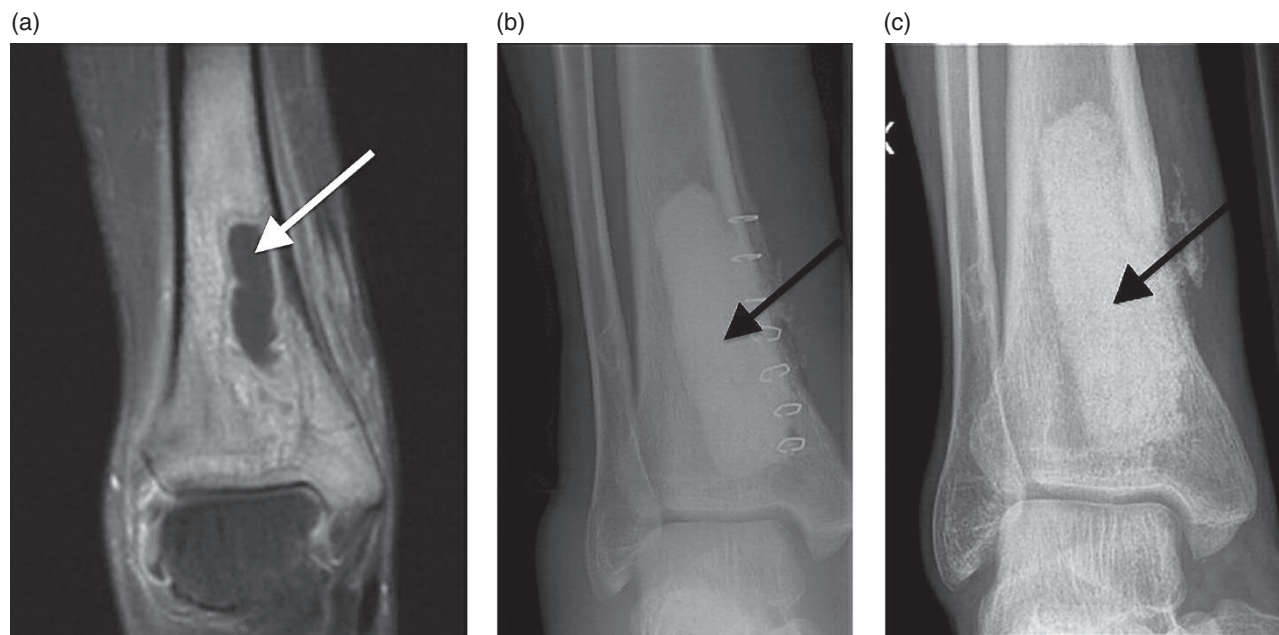


Figure 7 Healing of infection and inflammation of bone marrow (*osteomyelitis*) in human tibia with bioactive glass S53P4. (a) Preoperative magnetic resonance image (MRI) showing osteomyelitis (inflammation) in tibia (white arrow). X-ray images showing this bone cavity filled with bioactive glass S53P4 (black arrow) (b) directly post-operation and (c) at six months' follow-up. Source: Reproduced from [28] with permission from Elsevier.

autograft, the gold-standard bone graft. Using bioactive glass for the treatment of fractures in cortical (compact) bone is more challenging. Here, repositioning and fixation of the fractured parts is usually necessary, making the procedure more complicated. As vascular supply in compact bone is usually not as good as in cancellous one, ion release from the glass and its surface reactions are slower, and glass degradation and bone regeneration take longer [29].

Another orthopedic application concerns spinal fusion, whereby two or more adjacent vertebrae are joined to immobilize vertebrae and prevent movement caused by instability in some medical conditions, which can cause severe pain. A challenging factor here is the need to grow bone between two neighboring vertebrae. Good fusion rates have been achieved with bioactive glasses [29], and computer tomography analyses suggest that fusion rates and bone formation are comparable to those obtained with autogenous bone implants.

Bioactive glass S53P4 possesses antibacterial properties *in vitro*, which constitutes a great benefit for the treatment of *osteomyelitis*, an inflammation of the bone, which often leads to bone destruction. Conventional treatment combines implants (e.g. poly(methyl methacrylate) [PMMA] beads) with local administration of antibiotics; however, relapses occur in many cases (more than 20% for patients suffering from chronic *osteomyelitis*) [29]. In a multicenter clinical study, bioactive glass S53P4 (Figure 7) was well tolerated by patients suffering from *osteomyelitis*; the patients recovered quickly and no relapses occurred in any of them.

In another promising approach, bioactive glass and organic polymers make up composite materials, which combine the unique properties of bioactive glasses, such as controlled ion release and bioactivity, with the flexibility and low stiffness of polymers. Current commercial products combine a lactic acid copolymer (L-lactide-co-D,L-lactide) with Bioglass 45S5 particles in composites, from which degradable screws are produced for fixing ligaments. By reinforcing polymers with bioactive glass fibers, the composite stiffness can be tailored to match the requirements of the implantation site, potentially including load-bearing sites [8]; however, such products are not yet used clinically.

7.2 Scaffolds

Bioactive glass scaffolds having an open, interconnected porous structure are of interest for use as bone fillers for the *in situ* regeneration of bone, as they allow for cell ingrowth while the bioactive glass degrades, releasing modifier ions with therapeutic benefits. Porous scaffolds are also being investigated for tissue engineering applications, where a scaffold is seeded with cells *ex situ* before

being implanted. Unfortunately porous scaffolds are yet to become clinical products, as bioactive glasses currently having approval for clinical use (Bioglass 45S5 and BonAlive S53P4) crystallize readily during the sintering process.

An ideal scaffold will stimulate the body's natural regenerative mechanisms, recruit cells such as bone marrow stem cells, stimulate them to form new bone, and enable the formation of blood vessels within the newly formed bone. Pore diameters and connections need to be large enough to allow cells, tissue, and blood vessels to penetrate the structure, and the scaffolds need to support cell attachment and proliferation and guide tissue growth. If the scaffold degrades over time, it will be replaced by newly formed, natural healthy bone [1].

The common way to prepare scaffolds is to form glass particles (powder, granules, or short fibers) into the desired architecture and sinter the particles together. Surgeons prefer scaffolds to look like cancellous (spongy) bone, and several approaches have been used to achieve such structures. Methods include gel-cast foaming (whereby a gel is formed by *in situ* polymerization of organic monomers and the gel, after binding to the glass particles, is foamed prior to gelation; Figure 8a), the foam-replica technique (whereby a polymer, e.g. polyurethane, foam is coated with a bioactive glass slurry and burned out following the sintering step) and sintering of glass powder together with a soluble material, e.g. sodium chloride, which is dissolved later and leaves pores behind [31]. These methods allow for variation of pore size, pore size distribution, or interconnectivity. Mimicking cancellous bone, however, is not necessarily the best approach, depending on the intended application. Methods such as unidirectional freezing of bioactive glass suspensions or rapid prototyping [32] have been used to create scaffolds with oriented microstructures and greatly improved mechanical strength (Figure 8b and c).

In order to maintain scaffold properties such as mechanical strength and bioactivity, crystallization needs to be controlled during sintering. Bioactive glass scaffolds often are actually glass-ceramics rather than amorphous glasses, as the bioactive glass used (usually Bioglass 45S5) partially or fully crystallizes during the sintering. As this greatly reduces bioactivity and mechanical strength, bioactive glasses with improved processing, i.e. with a lower crystallization tendency, such as compositions 13-93 and ICIE16 (Table 1) are preferable [1, 10].

7.3 Dentistry

Most glasses and glass-ceramics used in dentistry tend to be inert (Chapter 8.5), with the exception of compositions used in glass ionomer cements, which set by a neutralization reaction between an acid-degradable fluoroaluminosilicate glass and a solution of poly(acrylic acid). In

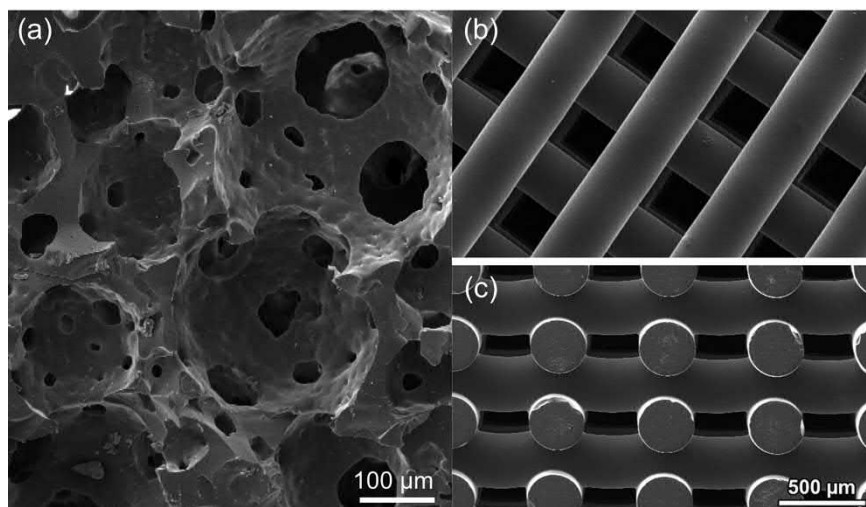


Figure 8 Scaffolds prepared from melt-derived bioactive glass by (a) gel-cast foaming (glass ICIE16) and (b, c) 3-D extrusion printing (glass 13-93). Source: (b, c) adapted from [30] with permission from Elsevier).

dentistry bioactive glasses are utilized either to treat bone defects or in oral care products (Section 7.4), but only a small number of commercial products are available. Bioactive glasses have also been implanted successfully in maxillofacial reconstruction surgery.

A large number of microorganisms are present in the oral cavity, where, together with other factors, they form a biofilm (the *plaque*) on the teeth. If not removed, this biofilm turns into *calculus* or *tartar*, a hardened dental plaque, leading to *gingivitis*, an inflammation of the gums. Gingivitis in advanced stages can give rise to *periodontitis*, an inflammatory disease affecting the tissue around teeth, where the gums recede from the teeth and the remaining pockets can become infected. If left untreated, this disorder can result in bone loss, loosening, and loss of teeth. Granules of Bioglass 45S5 (PerioGlas) have been used successfully to regenerate this bone and to promote new bone formation as well as the development of connective tissue in the periodontal area [29].

An early commercial application of bioactive glass in dentistry was filling extraction sockets to prevent the resorption of alveolar bone after tooth loss prior to placing a dental implant [8]. In early years, cones of Bioglass 45S5 were implanted into the alveolar sockets, whereas nowadays granular Bioglass is used instead to facilitate glass degradation and replacement by natural bone. Once the cavity has been filled and the jawbone regenerated, dental implants can be placed.

7.4 Oral Care

Fine bioactive glass (Bioglass 45S5) powder has recently been incorporated into commercial toothpastes for treating sensitive teeth. Dentine hypersensitivity is caused by dentinal tubules being exposed, thereby allowing external stimuli such as heat or cold to cause the sensation of pain.

Occlusion of these tubules has therefore long been recognized as the preferred treatment, which can be achieved by enhancing the natural process of apatite mineralization in the oral cavity. This is why most dentifrices treating dentine hypersensitivity contain ions, which aid in the precipitation of apatite, e.g. fluoride, strontium, phosphate, or calcium.

Bioactive glasses containing these ions also release them as soon as they are in contact with saliva in the mouth, causing supersaturation with regard to apatite. The original idea behind incorporating bioactive glass into toothpaste was that this would lead to apatite precipitation and the occlusion of dentinal tubules (Figure 9).

Recently, it has been recognized that toothpastes containing bioactive glass can also be used to remineralize enamel. In clinical trials a reduction in gingival bleeding, plaque growth, and an improved pain relief have been found when bioactive glass-containing toothpastes are used instead of control products. The success of these toothpastes has led to the development of new bioactive glass compositions, particularly fluoride-containing ones, which have been designed to stimulate the formation of fluoroapatite on the dentine, which is more resistant to acid attack than hydroxycarbonate apatite.

Other dental care applications of bioactive glass include the polishing of teeth by air-abrasion methods, a process that usually involves the use of particles such as sodium bicarbonate. According to patient reports, Bioglass 45S5 polishing results in a reduction in tooth sensitivity and also in whiter teeth than those treated with sodium bicarbonate [1].

7.5 Miscellaneous

Upon skin damage, in healthy individuals, a succession of different processes takes place to heal the wound. Within

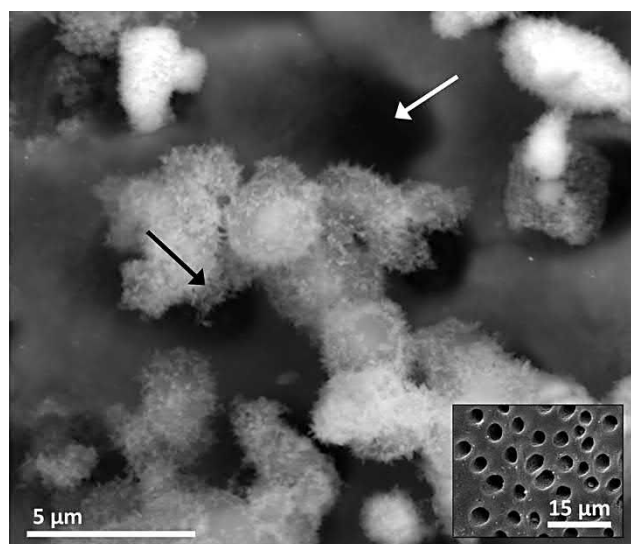


Figure 9 Scanning electron microscope images of a dentine disc at seven days in Tris buffer solution with fluoride-containing glass powder showing dentinal tubules (white arrow) partially blocked by apatite crystals (black arrow). Inset shows exposed tubules in dentine disc after etching with citric acid before storage in Tris buffer.

just minutes of the damage, the first step is blood clotting (*hemostasis*). Particularly in patients suffering from diabetes, however, wound healing can be slowed down dramatically. Elevated blood sugar levels cause narrowing of the blood vessels, decrease the blood flow, and thus reduce the transport of oxygen and nutrients to the wound. This leads to slow- or non-healing wounds, which greatly lower the quality of life for the patients. Wound dressings made from bioactive borate glass nanofibers (Mirragen®) are an effective treatment of diabetic wounds [8], most likely by enabling the formation of blood clots. As the borate glass fibers degrade with time, the wound dressing pads do not require removal during follow-up care.

Glass spheres used for the *in situ* irradiation of malignant liver tumors have a composition differing very much from those of the bioactive glasses discussed. They are designed to be very stable in physiological fluids to prevent leakage of radioactive isotopes from the target organ. But, like bioactive glasses, they are introduced into the human body as part of a medical treatment. For this reason, they also need to be discussed here. In radiation therapy, malignant tumors are exposed to ionizing radiation, which damages DNA and therefore kills the cancerous tissue. One of several radioactive isotopes used to treat cancer is ^{90}Y , a beta emitter, which is produced *in situ* by neutron activation of the naturally occurring stable isotope ^{89}Y in microspheres made by flame spheroidization from yttrium aluminosilicate glass. In 2000 these microspheres (TheraSphere® [8]) obtained FDA

approval for the treatment of inoperable liver cancer. They are injected into the liver of the patients via the hepatic artery. They remain in the liver, emitting beta radiation *in situ*. As the radiation is delivered locally, much higher doses can be given than by external source without risk of damaging healthy tissue.

In more mundane applications, bioactive glasses are incorporated into a range of personal care products. Bio-glass 45S5 (under the trade name Vitryxx®) and some phosphate-free compositions are used in cosmetics (e.g. eye shadow or face powder), skin care, and even hair care products such as relaxers for hair straightening.

Finally, soluble phosphate glass boluses (Cosecure™) containing elements such as zinc, cobalt, or selenium are applied in veterinary medicine [33]. These boluses are placed inside the rumen of cattle or sheep, where they dissolve over a period of up to six months, providing the animals with trace elements and preventing deficiency.

8 Perspectives

Bioactive glasses are currently being investigated for many more applications; owing to long procedures necessary for acquiring approval for the use as medical devices, however, some of them may not be used clinically for another one or two decades. Nonetheless, some promising concepts will be introduced here.

In conventional composites, inorganic (bioactive glass) and organic (polymer) macroscopic phases are combined. Hybrid materials (Chapter 8.9), by contrast, have generated much interest in recent years as they combine the inorganic and organic phase at a molecular level, which makes the individual components indistinguishable above the micrometer scale and causes the hybrid to behave as a homogeneous material (Chapter 8.9). Their covalent bonding between co-networks of organic and inorganic molecules is needed to optimize their properties. For example, there is no risk of failure at the inorganic/organic interface, which is commonly encountered in conventional composites. Another great benefit of hybrids is that they can have “dial in” mechanical properties, from that of a stiff glass to an elastic polymer, to match those of either bone or cartilage [1]. A difficulty here is that the mechanical properties are not controlled by conventional parameters, such as polymer molecular weight, but rather by the way the molecules fit and bond together, which makes predicting the mechanical properties a challenge. For biomedical applications, a great benefit is that degradation rates can be controlled via the structure and that biodegradable hybrids, which are broken down in the body, for example, by enzymatic action, can be obtained if biodegradable polymers are used.

To make hybrids, polymers are introduced into the sol-gel process prior to gelation. No elevated temperatures are required, and therefore the polymers survive the processing, and the sol-to-gel transition can be exploited to allow foaming or 3-D printing of scaffolds. Much research remains to be done, however, as hybrid synthesis and processing involve many variables and advanced chemistry. The route to clinical products will be long as these are a completely new class of medical devices.

As their hardness, stiffness, and brittleness are much more similar to those of hard than soft tissue, bioactive glasses have so far been applied to bone and teeth mostly. In the last two decades, however, interest has grown in soft tissue applications [23] in the form of either fiber meshes (cf. wound healing as described in Section 7.5) or polymer matrix composites containing bioactive glass particles so that mechanical properties such as stiffness are more similar to those of soft tissue.

An area where the use of bioactive glass particles is promising is the investigation of incontinence resulting from urinary tract infections [23]. A form of clinical treatment includes the injection of suspensions of either collagen particles or inert particles prepared from polytetrafluoroethylene (PTFE) into the bladder neck, with the aim of increasing urethral resistance. In animal experiments with bioactive glass particle suspensions instead, urethral resistance does also increase without any inflammatory reactions, but an additional advantage is that, unlike inert particles, bioactive glass particles do not migrate within the body, but bond to the bladder soft tissue instead.

Phosphate glass tubes (4 mm in diameter and a few centimeters in length) have been investigated for nerve repair by bridging nerve defects [34]. When in contact with aqueous solutions, P_2O_5 - Na_2O - CaO -(MgO) phosphate glasses can dissolve completely, and one can vary their solubility by several orders of magnitude by changing the glass composition [8]. They also allow for the incorporation and subsequent release of therapeutically active ions, similar to phosphosilicate glasses (Section 6). But, unlike those of bioactive silicate glasses, many phosphate glass compositions do not show biomineralization, i.e. apatite formation, which is an advantage for soft tissue applications. Results from animal experiments in sheep suggest that nerve regeneration with degradable phosphate glass tubes is similarly effective as conventional forms of treatment.

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8.5

Dental Glass-Ceramics

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1 Introduction

The term dental glass-ceramics refers to biomaterials used to repair any defects in the natural tooth structure in order to restore the natural chewing function in a wider variety of situations and in a much nicer aesthetic way than with the traditional metal-based dental restoration [1, 2]. For vital teeth, restoration includes inlays, crowns, bridges, and veneers. Devitalized teeth are also built up with these biomaterials but require an appropriate dental post. Such a dental post may, for example, consist of a ZrO_2 rod that has to be adapted with a glass-ceramic [1]. The application and indication range of these materials differs quite significantly from that of *bioactive* materials [1]. The latter are designed to grow together with bone tissue to form a bond that does not involve any connective tissue. The *restorative* biomaterials, in contrast, have to be bonded to the natural (vital or devitalized teeth) with an adhesive.

The authors will refer to [1] for a history of the development of these materials. Here we will just state that in the 1900s inorganic dental restoratives initially involved porcelains and sintered ceramics on a feldspathic basis [3–5]. With the development and introduction of glass-ceramics in the 1950s, it was possible to control nucleation and crystallization of glasses and to design special properties. Therefore metal restorations were veneered with glass-ceramics, and metal-free restorations were possible. Glass-ceramics fulfill a high aesthetic solution for dental restoration to meet the patients need.

Irrespective of their application, be it of a technical or medical nature, dental glass-ceramics are produced

from a base glass. This glass must contain all the inorganic and chemical components necessary for controlled nucleation and crystallization processes [1]. Here, *in situ* mechanisms are the most convenient ones to use: the glass-ceramics develops from the base glass solely through its exposure to a time–temperature program. A wide variety of processes involving temperature and time relationships are available for this purpose, some of which involve multiple stage reactions. This chapter on dental glass-ceramics will show the usefulness of first producing a product in the form of a primary glass-ceramics, which is subsequently transformed into the finished product.

Because the most important criteria that have to be fulfilled in the development of restorative dental glass-ceramics are the needs of the patient, these will be addressed in detail in our first section. Subsequently, the properties of dental glass-ceramics will be discussed. Finally, a few groups of materials will be presented to illustrate the various ways in which glass-ceramics are used in dentistry currently and in a near future.

Rather than listing all the existing types of biomaterials used, we will deal only with some for which we have a firsthand experience to ensure the accuracy of the account. But these will nonetheless illustrate the basic principles involved as also put to use by other companies, which are sharing a worldwide market volume estimated in 2015 at 1 billion US\$ for fixed partial prostheses (FDPs), including all ceramic as well as metal ceramic restorations. Along with Ivoclar Vivadent, the main producers of materials widely used in clinical practice are VITA Zahnfabrik (Germany) with feldspathic, lithium silicate, and leucite-based systems, Dentsply Sirona (United States and Austria) and GC Corporation (Japan) with lithium silicate and leucite-based systems, and Kuraray Noritake Dental (Japan) with leucite-based systems.

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2 History and Present Uses of Dental Glass-Ceramics

Since time immemorial patients whose teeth have been damaged by either caries or periodontal disease or by traumatic incidents and accidents have expressed a desire to have them repaired. In many cases, only part of a tooth has to be replaced so that the still functioning part can be maintained. Dental inlays, onlays, crowns, bridges, or veneers are used to repair such defects (Figure 1). In situations where a tooth has to be extracted completely and replaced, implants or dental bridges are indicated. These types of replacements have to mimic the appearance of the original tooth, which implies that their optical properties should match those of the natural counterparts, and assume all the masticatory functions of the structure. As a result, restorative materials must be as strong and tough as natural teeth, exhibit high or even unparalleled resistance to the oral environment, and demonstrate the same attrition as natural teeth to help protect the opposing teeth. Finally, it is desirable for the restorative material to have the same thermal properties and coefficient of thermal expansion as that of the natural dentition.

In addition to the needs of patients, the equally important requirements of dentists and dental technicians must be considered in the development of suitable dental restorative materials. For example, these include more economically efficient working methods, effective cementation techniques for bonding dental materials to natural tooth structure, and also the visibility of restorative materials in X-ray images (radiopacity).

The first glass-ceramics to incorporate a successful combination of optical and mechanical properties was

DICOR® (Corning Inc./Dentsply International, USA). The favorable properties of this material were achieved through the precipitation of tetrasilicic mica crystals, $\text{KMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$ [6, 7]. Since this glass-ceramics featured a silica-rich glass matrix in addition to the crystals, it could be formed in the molten state and shaped into any desired dental restoration, for example, inlays, onlays, and crowns. The glass matrix also imparted the material with desirable optical and translucent properties. This constituted a major advantage over the previously known dental materials. Moreover, since mica crystals demonstrate eminent cleavage properties [1], this glass-ceramics could be machined in addition to being shaped with a hot-melt process.

Glass-ceramics as well as organic composite materials and inorganic sintered ceramics (e.g. ZrO_2 based) have become very popular because they allow particular properties to be combined selectively. Over time, the properties of the initial glass-ceramics have been further developed and improved, and new ones have been effectively combined. Nevertheless, finding the correct combination of mechanical parameters and optical and processing properties has posed a considerable challenge. In many cases, an increase in the mechanical properties, that is, strength and toughness, resulted in a decrease of light transmission properties, which made the materials look dull and opaque. In some cases, they showed inferior chemical durability compared with that of natural teeth. These types of weaknesses had to be overcome in ways satisfying the requirements described in detail in the next section.

3 Properties of Dental Glass-Ceramics

3.1 Mechanical Properties

The main mechanical properties that need to be addressed are wear resistance (established with a chewing simulator) and strength, measured as the biaxial flexural strength (according to ISO 6872), the K_{IC} value (according to single-edge V-notched beam [SEVNB] method). As already emphasized, it is important that the mechanical strength and toughness of dental biomaterials match the parameters of natural teeth. This constraint applies to the biomaterials used to fabricate dental inlays and, in some cases, to dental crowns in the anterior region. Other parameters must be observed in the development of dental biomaterials used to produce crowns for posterior teeth or abutments on implants or even dental bridges. The mechanical properties of these biomaterials should be significantly higher than those of natural teeth. Given these requirements, it is obvious that various types of glass-ceramics

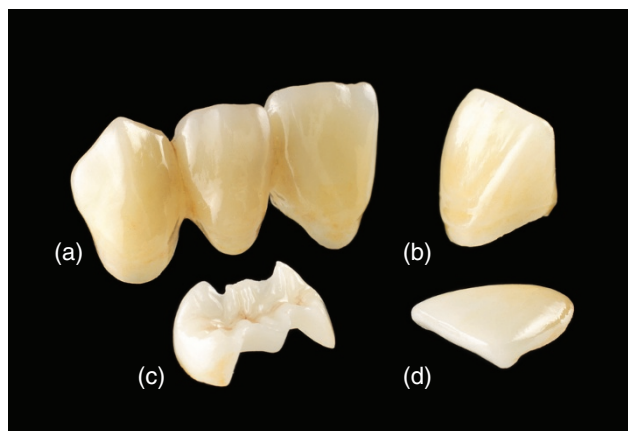


Figure 1 Glass-ceramics for dental restoration. (a) Dental bridge, lithium disilicate glass-ceramics veneered with an apatite glass-ceramic: IPS e.max® type. (b)–(c) Leucite glass-ceramics of IPS Empress® type. (b) Crown. (c) Inlay. (d) Veneer. Products of Ivoclar Vivadent AG, Liechtenstein. Reproduced from [1] with permission from Wiley.

are needed for different applications, as is the case with metal or rather steel. For example, materials used to fabricate dental inlays or crowns should exhibit, according to ISO6872, strengths and K_{IC} values higher than 100 MPa and $1.0 \text{ MPa m}^{0.5}$, respectively. By comparison, the strength and K_{IC} values of materials for dental three-unit anterior bridges should be higher than 300 MPa and $2.0 \text{ MPa m}^{0.5}$. These values could be achieved with glass-ceramics of a high crystal content and an interlocking microstructure.

3.2 Optical Properties

The optical property of light transmission or translucency is measured according to the British Standard BS 5612. Translucency is compared against a reference and established as a dimensionless number between 0 (zero), i.e. 100% light transmission of white light, and 1.0, a value indicating that the material is opaque so that any light does not pass through it. A desirable translucency for materials used in restorative dentistry lies between 0.5 and 0.8, depending on whether the tooth is vital or devitalized or anterior or posterior. This can be controlled in dependence of the crystal content and the corresponding microstructure.

3.3 Thermal Properties

The most important thermal parameters for dental materials are the coefficient of linear thermal expansion (CTE) and the thermal shock resistance. The desirable CTE parameters are higher than $10 \times 10^{-6} \text{ K}^{-1}$ (100–400 °C). In clinical situations, a dental material has to be resistant to thermal shock at temperatures between 37 °C (normal body temperature) and 50 °C or so (hot beverages) or even in the negative Celsius range upon consumption of ice creams. This property is closely analyzed in *in vitro* tests, and the material is optimized accordingly in terms of the glass composition and the microstructure. Furthermore, the material is tested in the chewing simulator, where the wear resistance compared with that of natural teeth is examined and the resistance to thermal shock is studied.

The resistance to thermal shock of a material should be tested not only with regard to the conditions in the mouth but also to the processing procedures followed by the dentist and the dental technician. It is often necessary for a material to withstand rapid temperature changes over a range of $\pm 100 \text{ K}$. The optimization of thermal shock resistance is a result of CTE control via the design of the microstructure of the glass-ceramics.

3.4 Chemical Properties

Like mechanical and thermal properties, the chemical durability of biomaterials can be determined by means of *in vitro* investigations. It is of utmost importance for the materials to be resistant to the acidic oral environment. The ISO 6872 norm on dental ceramic materials specifies that chemical durability must be tested in dilute acetic acid [CH_3COOH]. The resistance is measured as a loss of mass in relation to the surface. Depending on the application of the biomaterials, e.g. as a substructure with veneer or a non-veneered material, different limiting values apply, which range between 10 and $100 \mu\text{g}/\text{cm}^2$ and 100 and $2000 \mu\text{g}/\text{cm}^2$, respectively.

The aforementioned parameters refer to those that need to be fulfilled in the mouth of the patient. At the same time, the material has to demonstrate some etchability. This allows it to be treated with an acid in order to obtain a retentive surface, which will strengthen the bond to the tooth. Glass-ceramics do fulfill these requirements.

3.5 Radiopacity

Because the dental restoration must match the optical properties of natural teeth, the biomaterial may be difficult to distinguish from the real tooth structure. This *chameleon effect* makes the margin of the preparation blend in with the natural dentition, which causes, therefore, any contrast to disappear. For dentists, however, the preparation margins should remain visible in case the restoration needs to be removed. One can do it by incorporating certain radiopaque properties into the material, for example, by precipitating in the glass-ceramic $\text{Sr}_5(\text{PO}_4)_3\text{F}$ instead of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and Cs-leucite [$\text{CsAlSi}_2\text{O}_6$] (see Section 5 and reference [8]). These phases thus make the material structure look different from that of natural teeth in X-ray images.

4 Examples of Dental Glass-Ceramics

4.1 Leucite-Based Glass-Ceramics

The glass-ceramic IPS Empress® (Ivoclar Vivadent AG, Liechtenstein) is a dental restorative biomaterial, which can be either molded or machined. Its main properties are summarized in Table 1. This glass-ceramics has a chemical composition in the range of 59–63 wt % SiO_2 , 19–23.5 Al_2O_3 , 10–14 K_2O , 2.3–6.5 Na_2O , 0–1 B_2O_3 , 0–1 CeO_2 , and 0.5–3 CaO . Tetragonal leucite crystals [KAlSi_2O_6] constitute the main crystal phase [1]. This framework aluminosilicate displays characteristic Q^4 ($\text{SiO}_{4/2}$ and $\text{AlO}_{4/2}^-$, cf. Chapter 2.4) structural units in

Table 1 Properties of IPS Empress® CAD (scientific report of November 2006, Ivoclar Vivadent AG) and IPS e.max® CAD (scientific report of March 2011, Ivoclar Vivadent AG).

	IPS Empress® CAD	IPS e.max® CAD
Biaxial flexural strength (MPa)	>160	>360
K_{IC} (MPa m ^{0.5})	1.3	>2.0
Translucency	0.4–0.7	0.4–0.8
Coefficient of thermal expansion (CTE) (10 ⁻⁶ /K)	17–18	10–11
Chemical durability (μg/cm ²)	<100	<50

its structure (Figure 2a). The growth of this crystal phase begins with a typical surface nucleation process, which is initiated at the surface of the glass grains through tribochemical activation. The subsequent nucleation process proceeds inward from the surface. For this manufacturing step, monolithic glass-ceramics are produced as powder compacts.

The processes of nucleation, crystallization, and simultaneous sintering that are involved in the manufacture of the final product are clearly very complex. The microstructure of this leucite glass-ceramics (Figure 2b) shows a typical characteristic of leucite crystals, that is, polysynthetic twinning [1]. All crystals show this twinning effect in their growth. Depending on the desired translucency level, the growth process, which is diffusion controlled, can be frozen in order to achieve the required properties, especially to control the high CTE.

The molding procedure is a very special Ivoclar Vivadent AG invention. Today, this technology is widely used also by other companies. In contrast to hot melting, the viscous flow takes place in a higher viscosity range and, thus, at lower temperatures. Because the viscosity of the material in this flow process is approximately 10¹¹ Pa-s, dental restorations such as inlays, onlays, and crowns can be fabricated with the lost-wax technique whereby the viscous ceramic is pressed into an individually created mold made of a special *investment material*. Thanks to these lower temperatures, reactions with the investment material are significantly reduced with this method compared with the hot-melt technique.

Surprisingly, the IPS Empress® glass-ceramics can also be machined, thanks to the microstructure of the glass-ceramics.

4.2 Lithium Disilicate Glass-Ceramics

The glass-ceramic IPS e.max® CAD and Press (Ivoclar Vivadent AG, Liechtenstein) was developed with the aim of producing a stronger material than IPS Empress® to be used to fabricate dental bridges and abutments. This was achieved through precipitation of high amounts of lithium disilicate crystals [Li₂Si₂O₅], whose structure is shown in Figure 3a. These glass-ceramic systems show a high nucleation and crystallization rate [1].

Although Li₂Si₂O₅ is a layer silicate, these crystals do not have any cleavage properties. Van der Waals forces are usually invoked for crystals such as graphite or talc for which they determine their very weak interplanar bonding. For other structures, cleavage and cleavage energy are determined by the planes of lowest

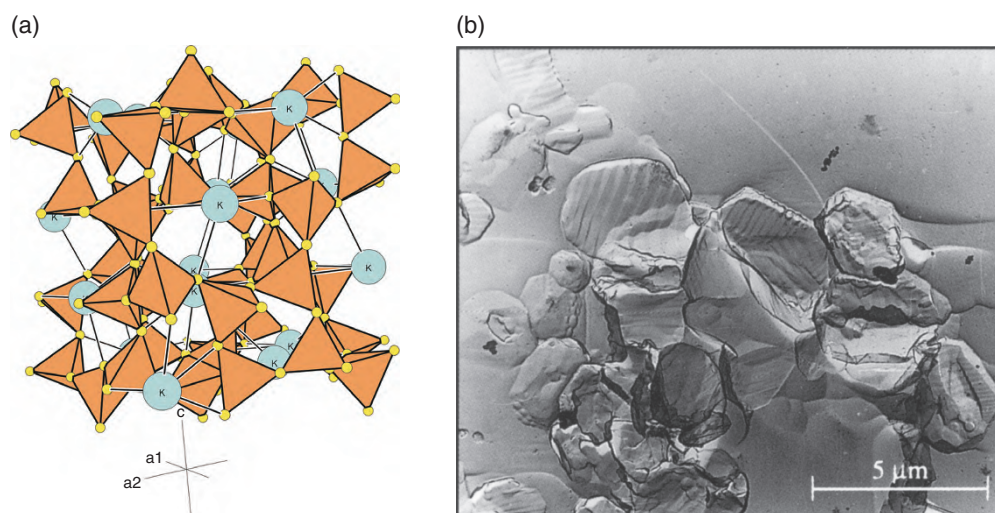


Figure 2 Leucite-based glass-ceramics used in IPS Empress®. (a) Crystal structure of leucite with the 3-D connection of corner-sharing [SiO₄]²⁻ and [AlO₄]²⁻ tetrahedra and the insertion of potassium ions. (b) Transmission electron microscopy micrograph of a replica of the microstructure. 2a: Reproduced from [1] with permission from Wiley. 2b: reproduced from W. Höland and M. Frank, Ivoclar Vivadent Report 10 (1994) 3–8. with permission from Ivoclar Vivadent AG.

ionic or covalent energy throughout the crystal; see, for example, [9].

In 1959, the first glass-ceramics was developed by Stookey in the form of a lithium disilicate glass-ceramics [1, 10]. This system was used to carry out extensive investigations on the stoichiometric relationships of the main components. Furthermore, new products were developed on the basis of this system [11–13]. Significant improvements of the properties of this type of glass ceramics were made by Beall [14] and Echeveria [15]. The glass-ceramic system was modified to produce a nonstoichiometric multicomponent system.

The development of biomaterials for dental restoration is also based on multicomponent systems. An important research result was the development of IPS e.max® in the preferred composition range of 64–73 wt % SiO_2 , 13–17 Li_2O , 2–5 Al_2O_3 , 0.5–5 K_2O , and 2–5 nucleating agent (preferably P_2O_5) [1, 2]. The most important scientific finding in the process was that, in this multicomponent system, the nucleation center was not in the form of a heterogeneous substrate or a metal colloid. Instead, the amorphous phase boundary between an amorphous phosphate phase and the glass matrix formed the starting point for the formation of the primary phase [1].

The microstructure of the IPS e.max® CAD and Press glass-ceramics is characterized by its interlocked nature and a high crystal content of more than 50 wt % (Figure 3b). The properties shown in Table 1 are achieved by the inorganic chemical composition and the particular microstructure of the glass-ceramics [1]. These properties allow the biomaterial to fulfill the requirements of restorative dental crowns (for anterior and posterior teeth, including molars) and dental bridges (in anterior teeth and up to the second premolar).

In order to facilitate machining of the IPS e.max® CAD glass ceramics according to the method described

for IPS Empress®, this material is cut in an intermediate “soft” state. For this purpose, the material is initially crystallized up to the lithium metasilicate (Li_2SiO_3) glass-ceramic stage. Lithium metasilicate is a chain silicate consisting of Q^2 (SiO_4 tetrahedron of two bridging and two non-bridging oxygen ions) structural units (Chapter 2.4). This type of glass-ceramics is easy to machine. After the material has been milled into the desired shape (e.g. dental crown), it is heat treated for a second time. In this process, the lithium disilicate acquires its final state of an interlocking crystal morphology.

4.3 Phosphate-Containing Glass-Ceramics

Another interesting material is made up of fluorapatite glass ceramics. Fluorapatite crystals $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ are orthophosphates that are built up out of isolated $[\text{PO}_4]^{3-}$ tetrahedra in typical Q^0 ($[\text{PO}_4]^{3-}$ tetrahedron of four non-bridging oxygen ions) structural units [1]. This crystal structure is shown in Figure 4. The nucleation process is controlled by a liquid–liquid phase separation. As a result, volume nucleation is initiated. The crystal growth process shows some very special features. The crystallization of the apatite phase, compared, for instance, with that of mica–apatite glass ceramics [1], proceeds in needlelike form. This particular growth process is typical of Ostwald ripening [1, 16, 17], which is known to yield a crystal morphology favorable to translucency. This type of biomaterial with its CTE of $9.5 \times 10^{-6} \text{ K}^{-1}$ and low sintering temperature of 750°C , therefore, can be used to veneer lithium disilicate glass-ceramics (Figure 1a) as well as ZrO_2 frameworks in restorative dentistry.

Besides, needlelike fluorapatite crystals can be simultaneously precipitated with leucite crystals in one glass-ceramic. This nucleation/crystallization process in which

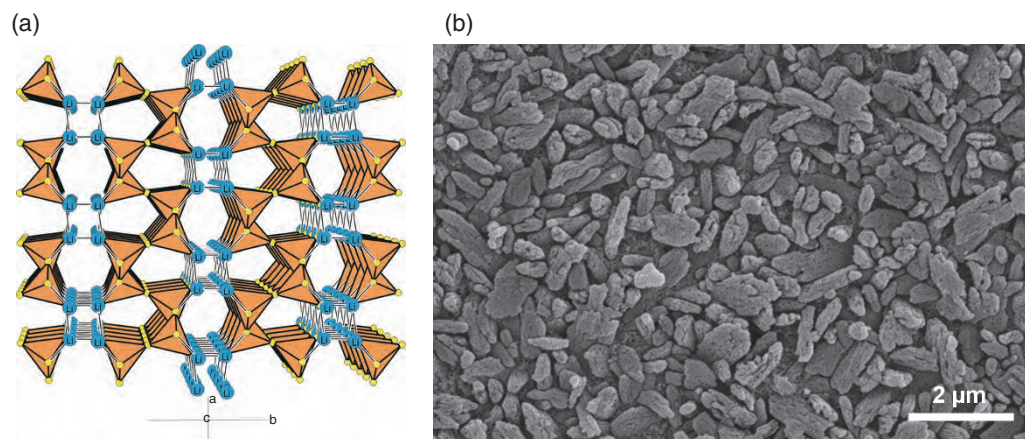


Figure 3 From crystal structure to glass-ceramics. Reproduced from [1] with premission from Wiley. (a) Structure of crystalline lithium disilicate as a layer silicate. (b) SEM micrograph of the microstructure and etched sample of lithium disilicate glass-ceramic. Reproduced from Höland et al. *J. Non-Cryst. Sol.* (2006) 4041–4050, with permission from Elsevier.

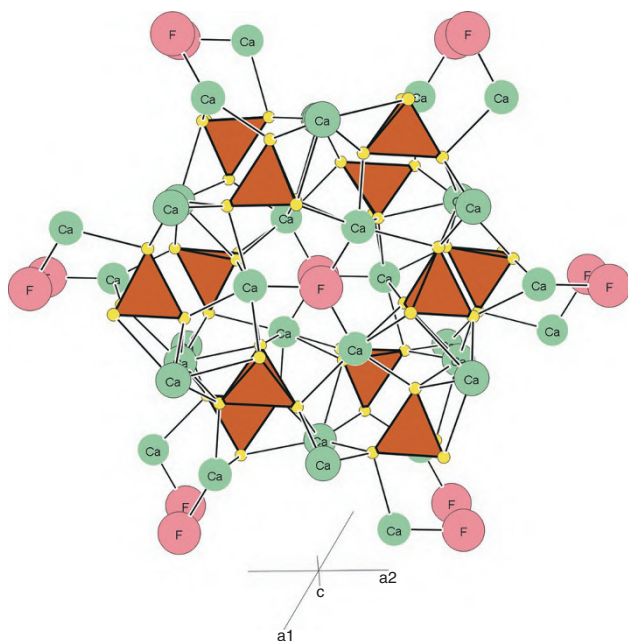


Figure 4 Crystal structure of fluorapatite. Reproduced from [1] with permission from Wiley.

two crystal phases are grown (according to two different mechanisms) is known as *twofold nucleation and twofold crystallization*. These mechanisms have been successfully used to develop IPS d.SIGN® (Ivoclar Vivadent AG), for example, which serves to cover up metal frameworks (e.g. of multiunit dental bridges).

In 2015, Ivoclar Vivadent AG, Liechtenstein, introduced a newly developed glass-ceramics called IPS Style® Ceram. This product contains silicate-type oxyapatite crystals in addition to needlelike fluorapatite crystals. In contrast to calcium fluorapatite, the abovementioned orthophosphate, this phase is formed as a silicate crystal (nevertheless, with similar structural units as those of the phosphate phase, [18]) according to the mechanism of surface nucleation and surface crystallization.

5 Perspectives

The development of state-of-the-art materials for restorative dental applications will continue to focus on combining optimally different properties. Consequently, the processes of controlled crystallization must be further improved and optimized. For this purpose, the mechanisms of twofold nucleation and crystallization also need to be finely tuned [8].

Furthermore, ongoing advances in the field of digital dentistry will present new challenges in the development of new materials, particularly in terms of the enhancement of the optical properties of dental materials and

the refinement of processing techniques. As shown in [2], glass-ceramics fulfill the patient needs with high aesthetics and different properties, such as mechanical, thermal, and chemical, to allow the use of the material as dental restoratives as dental crowns, veneers, inlays, and bridges.

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8.6

Relaxation Processes in Molecular Liquids

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1 Introduction

The formation of glasses is ubiquitous in nature and technology, yet a full microscopic understanding of the phenomenon is still lacking. When a liquid is cooled without crystallization below the melting point T_m , its viscosity increases strongly, but continuously by about 15 orders of magnitude until it reaches values of an amorphous solid at the glass transition temperature T_g . This viscosity increase is associated with a tremendous slowdown of the structural (α -) relaxation on a molecular level, which ceases on typical experimental timescales at T_g , so the configuration is arrested and the system falls out of thermal equilibrium (Chapter 3.7).

As exemplified by oxide melts, *associated* liquids have complex structures that keep constantly rearranging and, therefore, lack long-lived structural entities. Differences in bond strengths do exist and lead, for instance, to distinguish network-forming and network-modifying ions whose respective dynamics progressively decouple upon cooling. The dynamics of the liquid as a whole is controlled by that of the network formers, however, with the consequence that the glass transition takes place when the mobility of these ions becomes successively slower.

Like polymers (Chapters 8.7 and 8.8), *molecular* liquids present a different picture. As indicated by their name, they possess well-defined structural entities as a result of large differences between intra- and intermolecular bonding. Of particular importance then are the rotational degrees of freedom that often can be easily accessed experimentally. The relevance of rotational dynamics is

most simply illustrated by *plastic* or *glassy* crystals in which molecules rotate within crystalline networks at high enough temperatures and freeze in upon cooling in random orientations with the phenomenology of the glass transition.

Such rotations also take place despite the abovementioned structural differences in molecular and network glass formers alike, but, as opposed to plastic crystals, within disordered and kinetically rearranging frameworks. In molecular liquids, molecular reorientations like viscosity display strong deviations from Arrhenius laws for the temperature dependence of α -relaxation. It remains a great challenge to explain this feature, which is not accompanied by obvious changes in liquid structure. For this purpose, it is not sufficient to study the glass transition in a narrow sense, i.e. to focus on phenomena near T_g like aging, but it is necessary to explore what is nowadays more generally called the *glassy dynamics* in a wide temperature range from its onset above T_m down to T_g [1, 2].

A first topic addressed in this chapter thus is how comprehensive characterization of the molecular slowdown requires to cover a broad dynamic range. Accordingly, numerous studies have exploited techniques like dielectric spectroscopy (DS) [3] nuclear magnetic resonance (NMR) [4], depolarized light scattering (DLS) [5], and optical Kerr effect (OKE) [6], because they provide access to rotational motions related to the glassy dynamics whereas single-particle as well as collective displacements can be accessed by neutron scattering [7]. Besides, broadband mechanical relaxation experiments have recently become feasible [8]. These methods work in the time or the frequency domains to probe either *correlation functions* (Chapter 2.2) or *dynamic susceptibilities*, which characterize the amplitudes of spontaneous fluctuations around the average value of the respective observables.

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For direct comparisons, it is thus beneficial to transform the respective data to a common representation.

The second point to be dealt with here is the temperature dependence of relaxation processes, i.e. the correlation functions or dynamic susceptibilities change upon cooling. For simple liquids well above T_m , the correlation functions decay in one step with temperature dependences that obey Arrhenius laws. Upon cooling, the glassy dynamics emerges and leads instead to two-step decays, which are found for inorganic glass-forming liquids like silicate melts as well [9]. They can be attributed to a temporary caging of structural entities by their neighbors in dense liquids. Whereas the first decay results from the *rattling* of these entities within the cages, the second reflects their escape from them and, thus, the α -relaxation. A characteristic feature of α -relaxation is that it is non-exponential or, equivalently, that it has a non-Debye nature because it cannot be described by a Lorentzian susceptibility. At least in a first approximation, the temperature dependence of the time constant, $\tau_\alpha(T)$, is often described with the empirical Vogel–Fulcher–Tammann (VFT) equation (Chapter 4.1). Other representations have proven useful, whereas much effort is also currently devoted to describe the pressure dependence of τ_α .

In a third part of this chapter, attention will be paid to the theories that have been proposed to rationalize the glassy slowdown, referring to available reviews for more detailed accounts [10]. The mode-coupling theory is a first-principles approach that provides detailed predictions for the shape of susceptibilities [11]. It captures many aspects of the onset of the glassy slowdown as demonstrated by experimental and simulation studies made in the last decades. In its original form, it predicts a divergence of τ_α at a critical temperature T_c , which turns out to be substantially higher than T_g . This problem has been addressed by a generalized mode-coupling theory aiming at reproducing the non-Arrhenian slowdown in the deeply supercooled regime. Other more phenomenological theories of the glass transition assume that the increasing temperature dependence of the α -relaxation results from growing length scales related to dynamical or structural properties of the liquid. The long-standing history of this concept dates back to Adam and Gibbs (Chapter 4.1) who proposed that cooperatively rearranging regions grow upon cooling. Various kinds of spatial heterogeneity form also the cornerstones of current theories such as the frustration-limited domain approach, the dynamic-facilitation concept, or the random-first-order transition theory [10]. Furthermore, elastic models of glass-forming liquids have been proposed. For example, the elastically cooperative activated barrier hopping theory [12] presumes that the α -relaxation involves coupled local

hopping and collective distortions of the local environment, resulting in two related but distinct energy barriers. As a matter of fact, the quest for a characteristic length scale is a major topic in experimental and computational approaches.

In the fourth part of this chapter, the focus will be put on binary glass-forming liquids, which are of great importance in various fields. Prominent examples range from polymer blends and mixtures of water with small molecules, where the molecular species often show comparable mobility, to polymer–plasticizer and protein–solvent systems with a high dynamical asymmetry. In view of the omnipresence of such mixtures, it is natural to proceed from neat to binary systems. In doing so, the established relaxation phenomenology of the neat counterparts is very useful for an interpretation of the even richer dynamical scenarios of binary glass formers, where the more mobile component can, for instance, undergo a glass transition in a disordered frozen matrix formed by the less mobile component. Vice versa, mixing often allows one to separate diverse relaxation features of neat systems, paving the way for more detailed studies.

The penultimate feature that will be discussed is the secondary (β -) relaxation that emerges when T_g is approached and eventually governs the overall relaxation in the glassy state. A prominent example is the Johari–Goldstein (JG) β -relaxation, which often splits off from the α -relaxation in the highly viscous regime to manifest itself even below T_g . Other relaxation phenomena in the glass state ($T < T_g$), however, in particular at cryogenic temperatures, are beyond the scope of this review. Finally, the particular case of glassy crystals will be described. Here the translational degrees of freedom exhibit crystalline order, whereas solely the rotational degrees of freedom show a glass transition, which makes it possible to consider them as model systems in studies of the glassy dynamics.

Acronyms

DLS	depolarized light scattering
DS	dielectric spectroscopy
FTS	frequency–temperature superposition
JG	Johari–Goldstein
NMR	nuclear magnetic resonance
PCS	photon correlation spectroscopy
QENS	quasi-elastic neutron scattering
VFT	Vogel–Fulcher–Tammann

2 From the Boiling Point Down to the Glass Transition

2.1 Evolution of the Dynamic Susceptibility

In the frequency range 10^{-2} – 10^9 Hz, DS was and remains the most convenient method to characterize the dynamics of viscous liquids close to T_g [3]. Thanks to recent technical progress in the GHz–THz regimes, it has even become possible to cover the full spectral range of the dynamics of molecular liquids as illustrated by spectra recorded for glycerol [$C_3H_8O_3$] at different temperatures (Figure 1a) [3, 13]. Manifesting itself as a rather narrow peak, the primary or α -relaxation shifts to lower frequencies upon cooling, whereas a susceptibility minimum develops between the α -peak and the microscopic dynamics at highest frequencies, which includes the boson peak (Chapter 3.4, Section 6). This gap is filled by secondary relaxation processes that emerge as a fully developed β -peak or as an *excess wing* described by a $\omega^{-\gamma}$ power law (like in glycerol) [14]. Both types of relaxation survive below T_g . Because the α -peak itself cannot be described in terms of the single dielectric relaxation time of the Debye model, the Cole–Davidson function is often used to account for asymmetric peak broadening, explicitly, in terms of the complex susceptibility:

$$\chi_{\alpha}^*(\omega) = \frac{\Delta\chi_{\alpha}}{[1 + i\omega\tau_{CD}]^{\beta_{CD}}}. \quad (1)$$

Likewise, the Kohlrausch function is commonly employed to consider the non-exponential time dependence of the α -relaxation:

$$C(t) = \Delta\chi_{\alpha} e^{-(t/\tau_K)^{\beta_K}}. \quad (2)$$

Here, $\Delta\chi_{\alpha}$ denotes the relaxation strength, τ_i the characteristic time constant, and β_i the corresponding stretching parameter.

Beginning with the pioneering work of Cummins and coworkers [5], broadband DLS in the GHz–THz range with a double monochromator and tandem Fabry–Pérot interferometry has become another useful tool even for inorganic glasses [15]. The information obtained complement the DS dynamic susceptibility data, in particular at high temperatures, although it should be kept in mind that DS probes a rank-one rotational correlation function $C^{(1)}(t)$, whereas DLS (and NMR) probes a rank-two function $C^{(2)}(t)$, so systematic differences may occur. For ethylbenzene [C_8H_{10}], the spectral features observed by DLS (Figure 1b) are nonetheless similar to those derived from DS. Close to boiling point (T_b), the susceptibility minimum disappears, and the α -relaxation merges with the microscopic peak to become essentially a single maximum.

After transformation into the time domain, DLS data can be complemented by results from photon correlation spectroscopy (PCS), which probes molecular reorientation at longer timescales as exemplified by measurements made on m-tricresyl phosphate [$C_{21}H_{21}O_4P$] (Figure 2) [16]. The resulting evolution of the correlation function monitored over sixteen decades is best suited to summarize the general properties of glassy dynamics. These are (i) the two-step correlation function emerging upon cooling of a liquid from T_b ; (ii) its long-time decay showing relaxation stretching; (iii) the degree of stretching being virtually constant with decreasing temperatures down to T_g , so time– (or frequency–) temperature superposition (FTS) can be considered to apply; and (iv) the non-Arrhenian temperature dependence of the time constant $\tau_{\alpha}(T)$ (see below).

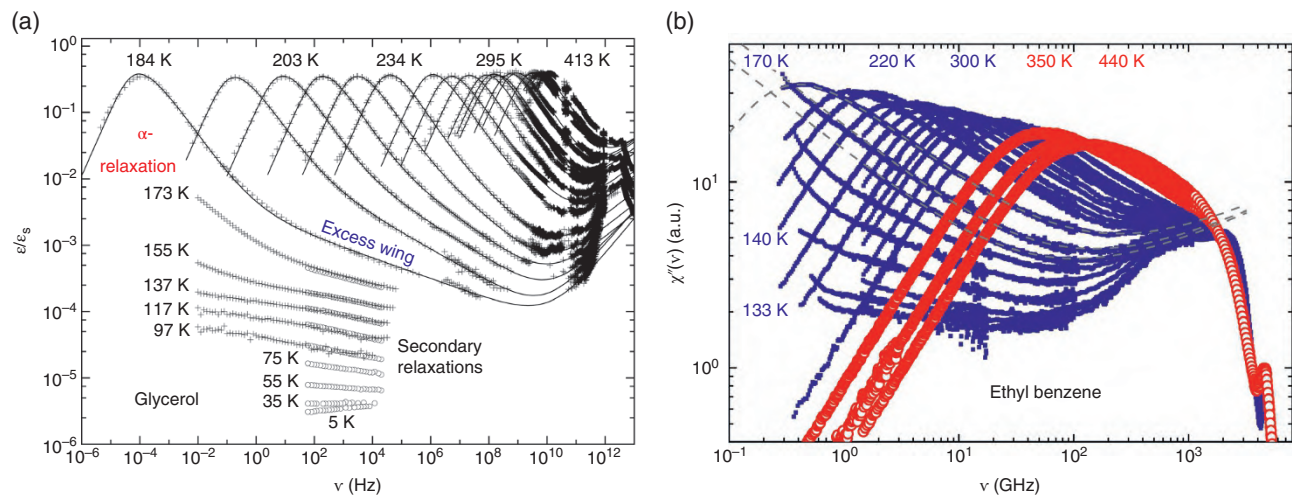


Figure 1 Relaxation in molecular liquids at different temperatures. (a) Normalized dielectric susceptibility of glycerol ($T_g = 186$ K) [3, 13]. Solid lines: interpolations by a phenomenological model. (b) Depolarized light scattering spectra of ethylbenzene ($T_g = 115$ K) below (blue/black) and above (red/gray) the boiling temperature ($T_b = 416$ K). Dashed lines: interpolation by mode-coupling theory. Source: Reprinted with permission from Ref. [16]. Copyright 2013 AIP Publishing. (See electronic version for color figures.)

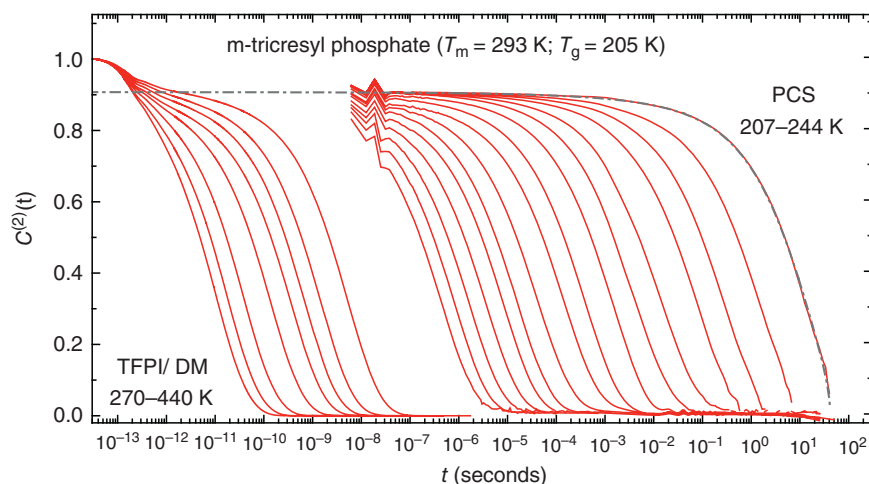


Figure 2 Crossover from simple dynamics at highest temperature to glassy dynamics at low temperatures: rank-two reorientational correlation function $C^{(2)}(t)$ of m-tricresyl phosphate as observed from double monochromator and tandem Fabry-Pérot interferometry (DM/TFPI) after Fourier transformation and from photon correlation spectroscopy (PCS). Dashed lines: fit by a Cole-Davidson function. Source: Adapted with permission from Ref. [16]. Copyright 2013 AIP Publishing.

The first step in the correlation function reflects all kinds of fast dynamics, including the aforementioned cage rattling. Once glassy dynamics is established, no further change of the basic shape of the correlation function thus appears to be observable upon cooling. Such glassy dynamics is established well above T_m , which implies that simple liquid dynamics with a mono-modal correlation function and Arrhenius temperature dependence are if at all only found near T_b . In other words, glassy dynamics in the sense defined here is not restricted to the super-cooled regime, but is characteristic of dense liquids. In this respect, it is worth emphasizing that mode-coupling theory [11] essentially reproduces the onset of these relaxation features [7, 16].

The approximate validity of FTS for the α -process and excess wing of the susceptibility of glycerol is illustrated (Figure 3a) by the single master curve $\chi''(\omega\tau_\alpha)$ derived from DLS and DS broadband data and results from ^1H NMR relaxometry [16]. Although the excess wing is difficult to identify in the time domain because of its small relaxation strength, it is well recognized in the frequency domain. In the high-frequency regime of the excess wing, the DLS and DS susceptibilities are related by $\chi''_{(2)}(\omega) \cong 3\chi''_{(1)}(\omega)$. This difference can be rationalized in terms of small-angle reorientation, implying that the excess wing represents a spatially highly hindered motion and probably is a generic feature of molecular liquids [16].

Molecular glass formers have also been investigated by OKE experiments [6], which probe the same fluctuations as DLS through the changes in the refractive index of a material induced by an applied electrical field. The experiment monitors the pulse-response function $F_{\text{OKE}}(t) \propto -(\text{d}C^{(2)}(t)/\text{d}t)$ in a rather wide time window. This representation of the data is particularly useful for an identification of different power law regimes contained in the main correlation loss. Regarding the α -relaxation peak and the excess wing, their short-time power law exponents β and γ reappear as $F_{\text{OKE}}(t) \propto t^{-(1-\beta)}$ and

$\propto t^{-(1-\gamma)}$, respectively. For liquids as diverse as benzophenone [$\text{C}_{13}\text{H}_{10}\text{O}_1$], glycerol, and m-tricresyl phosphate [$\text{C}_{21}\text{H}_{21}\text{O}_4\text{P}$], two power laws are seen (Figure 3b) at shorter and longer times, the latter being the high-frequency part of the α -process. Although the first has been termed the intermediate power law [6], it appears to be nothing else but the excess wing as demonstrated in Figure 3b where the DS and PCS data included also show a second power law at short times [16].

The effect of pressure on the susceptibility spectra has also been investigated thoroughly [17]. It turns out that the susceptibility spectra of many glass formers (except hydrogen-bonded systems) are similar in the region of the α -process if the different P and T of the measurement are selected so as to ensure the same values of τ_α . This fact is not a surprising if one assumes that FTS is a generic feature of the glass transition, i.e. that relaxation stretching is not altered by changes in T or P . From 50 °C and 0.1 MPa to 90 °C and 215 MPa (Figure 4) [17], this *isochronal superposition* of α -relaxation is nicely illustrated by the dielectric spectra of phenolphthalein dimethylether [$\text{C}_{22}\text{H}_{18}\text{O}_4$].

Altogether, various experimental techniques yield a consistent picture for the evolution of the dynamic susceptibility associated with the rotational dynamics of molecular liquids approaching T_g . These findings are complemented by results from neutron scattering, which probes equally well the corresponding displacement dynamics though in a significantly narrower dynamic range [7]. For some glass formers, a distinct secondary relaxation is not observed. Hence, changes in the spectral shape are dominated by the emergence of the excess wing on the high-frequency flank of the α -relaxation peak.

2.2 Time Constants

A major challenge posed by the glass transition phenomenon is to arrive at a consistent description of $\tau_\alpha(T)$ as obtained from different experimental techniques.

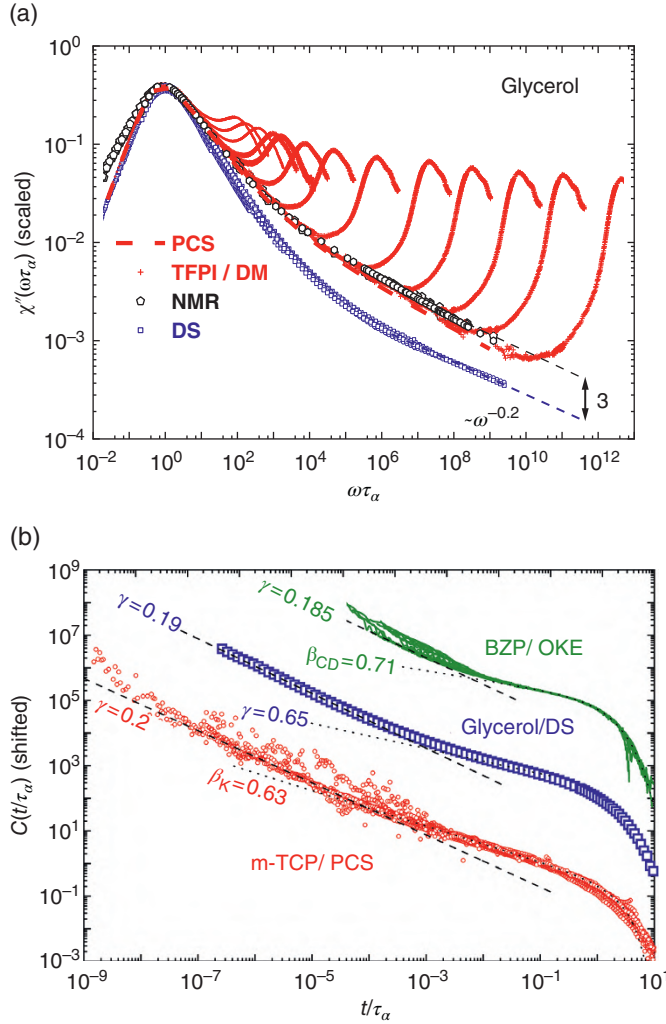


Figure 3 Relaxation in molecular liquids in different representations. (a) Dynamic susceptibility of glycerol as a function of reduced frequency determined by DS, field-cycling ^1H NMR, DLS (DM, double monochromator; TFPI, tandem Fabry–Pérot interferometry), and PCS; arrow indicates a factor 3 between the amplitudes of the excess wing. Source: Adapted from Ref. [16]. Copyright 2013 AIP Publishing. (b) Pulse-response representation of relaxation as a function of reduced time: two power laws seen for benzophenone (BZP) in optical Kerr effect (OKE) data [6], for glycerol in dielectric data, and for m-tricresyl phosphate (m-TCP) in PCS data; dashed lines indicate intermediate power law/excess wing; dotted lines reflect the α -process. Source: Adapted with permission from Ref. [16]. Copyright 2013 AIP Publishing.

Regarding molecular reorientation, however, various methods do yield comparable time constants. To describe their temperature dependence, the VFT formula is often applied in spite of high-temperature shortcomings and of doubts raised on the implied divergence of the correlation time at low temperatures. To test its validity, the VFT relation can be explicitly recast in terms of the fragility index m , T_g , and τ_∞ [18]:

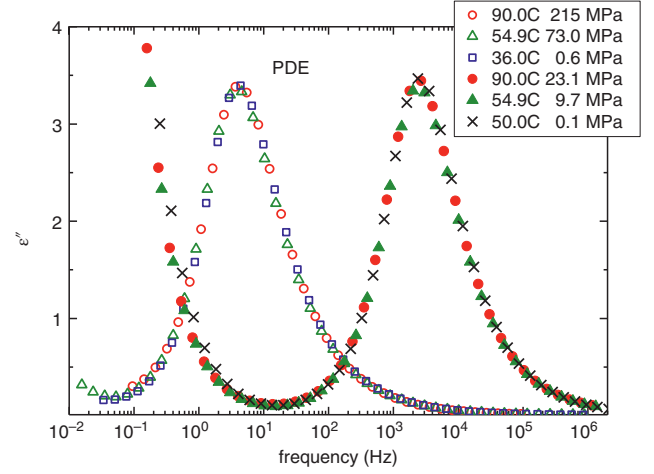


Figure 4 Relaxation at different temperatures and pressures: isochronal superposition. The spectral shape of the dielectric relaxation of phenolphthalein dimethylether (PDE) agrees for different pressure–temperature combinations yielding the same structural relaxation time τ_α . Source: Courtesy M. Paluch.

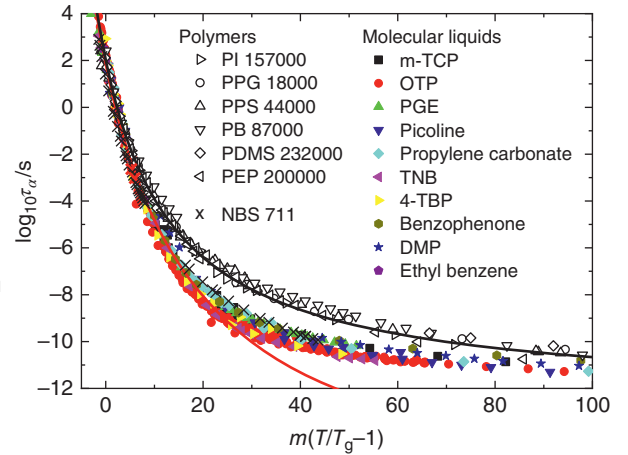


Figure 5 Reorientational correlation times of molecular liquids (solid symbols) and polymers (open symbols): experimental data and VFT fits (solid lines) made as a function of the reduced variable of Eq. (1), m being the fragility index. Scaled viscosity of the NBS 711 silicate melt included for comparison (cross).

$$\lg \frac{\tau_\alpha}{\tau_\infty} = \frac{K_0^2}{m(T/T_g - 1) + K_0}. \quad (3)$$

Here, $K_0 = \lg(\tau_\alpha(T_g)/\tau_\infty)$, whereas the parameter $m = \left. \frac{\partial \lg \tau_\alpha}{\partial (T_g/T)} \right|_{T=T_g}$ specifies the *steepness* at T_g in an

Angell plot $\lg \tau_\alpha$ vs. T_g/T . Comparisons made on the basis of Eq. (1) indicate that the VFT relation works well up to highest temperature for polymers but clearly fails for molecular liquids as well as for the NBS 711 standard silicate melt (Figure 5).

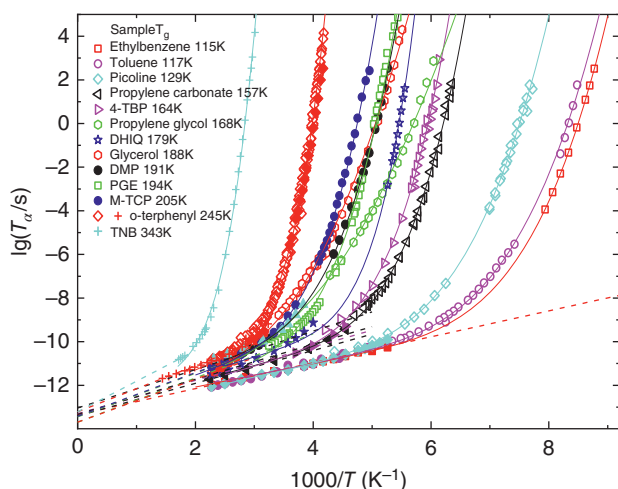


Figure 6 Reorientational correlation times of molecular liquids. (a) Arrhenius plots of data for molecular liquids with glass transition temperatures ranging from 115 to 343 K. Dashed lines: high-temperature Arrhenius fits. Solid curves: interpolations made with Eq. (4). Source: Reprinted with permission from Ref. [16]. Copyright 2013 AIP Publishing.

Many other approaches have been proposed to interpolate $\tau_\alpha(T)$, but none is widely accepted because molecular glass formers have been little studied above T_m , the available data being usually restricted to $\tau_\alpha(T) > 10^{-9}$ seconds. Yet, as already noted, susceptibility spectra and, thus, correlation times down to 10^{-12} seconds are now easily accessible by DLS. Such $\tau_\alpha(T)$ data obtained from DS and DLS/PCS measurements are thus especially valuable as they may cover the entire temperature range between T_g and T_b . Clearly, an Arrhenius law with the activation energy E_∞ is obeyed at higher

temperatures before the effective activation energy $E(T)$ strongly increases when T_g is approached (Figure 6). Although the quantity E_∞ must not be associated with some single-particle barrier in a liquid, one can take the high-temperature Arrhenius law as an empirical limit and decompose $E(T)$ into two parts, namely, $E_{\text{coop}}(T)$ and E_∞ [16]:

$$\tau_\alpha(T) = \tau_\infty \exp \left(\frac{E_\infty + E_{\text{coop}}(T)}{T} \right). \quad (4)$$

With the assumption that $E_{\text{coop}}(T)$ is an exponential function of temperature, one can then plot $E_{\text{coop}}(T)/E_\infty$ against T/E_∞ in a generalized Angell representation [16]. This analysis thus assumes that the energy scale of the glass transition is not set by T_g , but by the experimentally accessible high-temperature quantity E_∞ . Once the influence of E_∞ and $E_{\text{coop}}(T)$ is disentangled in this way, a new measure of fragility can be introduced. It is the steepness in $E_{\text{coop}}(T)/E_\infty$ vs. T/E_∞ plots, which clearly distinguishes a highly fragile liquid such as o-terphenyl [$\text{C}_{18}\text{H}_{14}$] from the much less fragile propylene glycol [$\text{C}_3\text{H}_8\text{O}_2$]. Whether the increase of $E_{\text{coop}}(T)$ or the apparent activation energy of $\tau_\alpha(T)$ is connected to some growing correlation length is a matter of recent experiments as well as theoretical considerations. Here two further points only will be noted. The first is that the phenomenological approach of Eq. (4) bears some similarity with the description introduced by the elastically cooperative activated barrier hopping theory [12]. The second is that diffusion data have to be excluded from the present discussion as they show a *decoupling phenomenon*, i.e. that the Stokes–Einstein relation (Chapter 4.3) is violated [19].

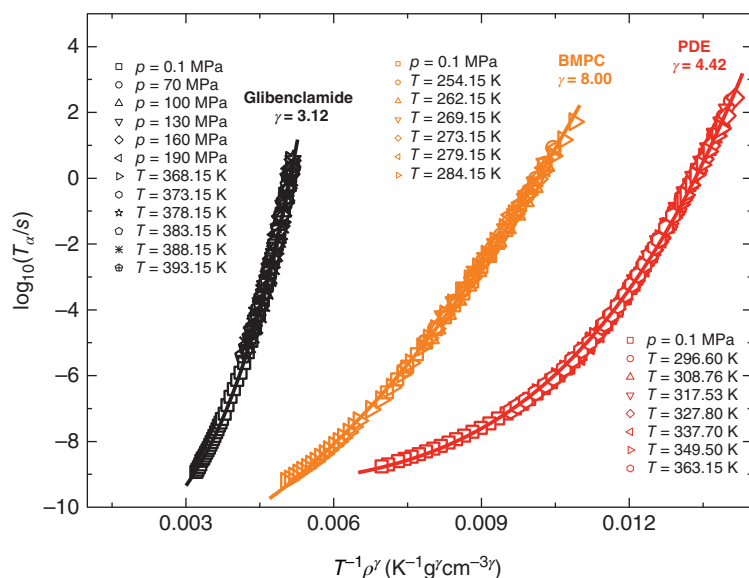


Figure 7 Relaxation times at different temperatures and pressures: temperature–density scaling of time constants τ_α as function of the parameter $X = \rho^\gamma/T$ for different molecular glass formers [17]. Source: Courtesy M. Paluch.

Attempts have been made to correlate the usual fragility index m with some other property of the liquid, for instance, the stretching parameter β , the Poisson ratio, or the so-called non-ergodicity parameter (relative amplitude of α -process) [2]. Yet, no correlation between m and β has been reported in recent surveys. Except for hydrogen-bonded liquids, the fragility actually varies only weakly among molecular liquids.

For deeper analyses, high-pressure measurements are in fact needed because lowering the temperature of a liquid at constant pressure causes at the same time a decrease in thermal energy and an increase of density, the contributions of which cannot be disentangled. Extensive measurements have thus been made at elevated pressure [17] to determine correlation times as a function of temperature and density, $\tau_\alpha(T, p)$, and to express them in terms of some scaling function $J(X)$. For $X = \rho^\gamma/T$ (Figure 7), an exponent $\gamma = 4$ can, for example, be derived for the Lennard-Jones potential (Chapter 2.8) when assuming an r^{-12} repulsive term and disregarding the attractive part. But the value of γ varies for different systems since this simple interaction potential is much too approximate for molecular liquids.

2.3 The Search for a Characteristic Length Scale

The dramatic increase of timescales in supercooled liquids has been assigned to growing length scales of heterogeneous and to collective structural rearrangements in many studies of the glass transition [1, 10].

Despite much research, however, the nature of the entities that determine this relaxation slowdown remains controversial.

It is well established that dynamical heterogeneities are key features of dense liquids [10, 19]. Computer simulations, in particular molecular dynamics (MD) simulations, have been a valuable tool to show that fast and slow particles are not randomly distributed in the weakly supercooled regime, but spatially correlated (Figure 8). The space–time characteristics of dynamical fluctuations have been evaluated in different ways. To quantify the amplitude of spontaneous fluctuations around the average dynamics, a four-point, time-dependent density correlation function and its volume integral, the generalized dynamic susceptibility $\chi_4(t)$, are commonly used [10]. The spatial correlations between the mobility of particles are of a transient nature, but they increase upon cooling, thus pointing to growing dynamic length scales.

Likewise, particles with high or low mobility form clusters, the sizes of which increase with decreasing temperatures. Such spatially heterogeneous dynamics has been reported not only for atomic and molecular systems [20, 21] but also for a model of silica melt [9]. As an example, MD simulations of a monoatomic liquid reveal an increasing spatial heterogeneity upon cooling in the form of a distinct maximum in the time-dependent mean size of clusters consisting of highly mobile particles (Figure 9a). In more detail, the highly mobile particles show a cooperative string-like motion [21] through which they follow one another along a one-dimensional

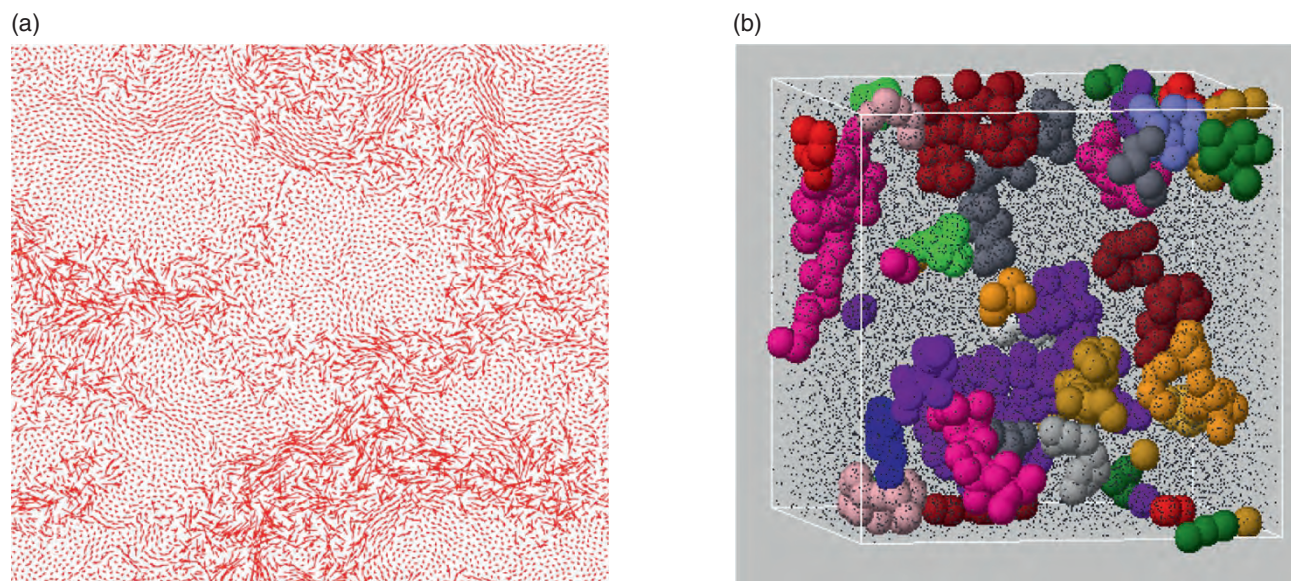


Figure 8 Molecular dynamics simulations of spatially heterogeneous dynamics in supercooled liquids. (a) Single-particle displacements in a glass-forming liquid in two dimensions during a time interval $t \approx \tau_\alpha$. Source: Reprinted with permission from Ref. [10]. Copyright 2011 APS. (b) Clusters of highly mobile particles in a monoatomic liquid distinguished by different hues; less mobile particles shown as dots. Source: Reprinted with the permission from Ref. [20]. Copyright 2004 APS.

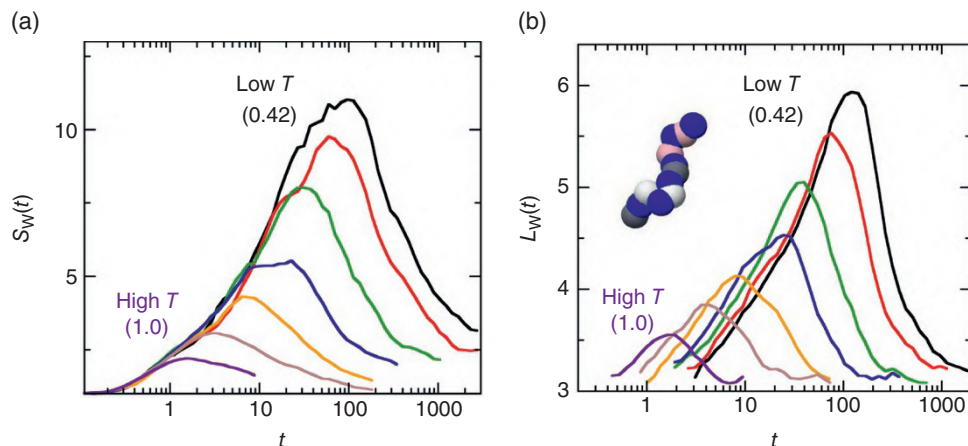


Figure 9 Molecular dynamics simulations of highly mobile particles in a monoatomic supercooled liquid at various temperatures [20]. (a) Time-dependent weight-averaged cluster size $S_W(t)$. (b) Corresponding string length $L_W(t)$. Inset: example of string-like motion, light and dark spheres visualizing the positions of the same particles at the beginning and at the end of a time interval with the string motion, respectively.

pathway. The time-dependent mean length of these strings grows upon cooling, implying that this cooperative motion becomes an important relaxation channel at low temperatures. The cluster size and the string length reach maximum values when the particles begin to escape from their local cages, so the clusters or strings may be involved in the elementary step of the α -relaxation. Accordingly, these entities have been considered as supporting the dynamic-facilitation concept [2, 10]. Whereas clusters are also considered to be key elements of the α -relaxation of silica melt, such strings are not relevant to this network-forming material.

Owing to computer limitations, these simulations are still restricted to high temperatures, say, $\tau_\alpha < 1 \mu\text{s}$. Challenging experimental work is thus required to follow the dynamic length scales down to T_g . In an NMR approach, 4-D cross-polarization experiments have yielded evidence for a spatially heterogeneous dynamics near T_g at a length scale of about 3 nm [10]. Likewise, a switch between fast and slow dynamical states has been observed by atomic force microscopy in regions that have a size of a few nanometers [10]. The temperature dependence of the dynamic length scale has also been recently addressed. Even though the four-point dynamic susceptibility still awaits direct measurement for viscous liquids, the experimentally accessible responses of correlation functions to temperature or pressure changes yield lower bounds of $\chi_4(t)$.

A growing dynamic length scale is indeed related to the glassy slow down as the maximum of the estimated $\chi_4(t)$ can be regarded as a measure of the number of molecules, N_{corr} , that are dynamically correlated at the timescale of the α -process. In the various liquids considered, a fast increase of N_{corr} at higher temperatures is followed by a slower growth at lower temperatures [22]: when the α -process slows down by roughly six orders of magnitude, N_{corr} increases by only a factor of 2 (Figure 10a).

Recently, it has been argued that the *a.c.* nonlinear dielectric response $\chi_3(\omega)$ opens another way for a determination of N_{corr} [23] because its maximum value would be a direct estimate of N_{corr} . Although the argument has been disputed, there is a simple relation between $N_{\text{corr}}(T)$ and the effective activation energy of the α -process, $E(T)$ (Figure 10b). This finding has been taken as evidence that the nontrivial temperature dependence of the glassy dynamics is caused by an increasing energy barrier arising from a growing number of cooperatively moving particles.

To determine length scales, another fruitful approach consists in studying liquids confined in very narrow spaces since deviations from bulk properties result as soon as a characteristic length scale is reached. But unambiguous analyses of such finite-size effects are often hampered by liquid–matrix interactions, i.e. interface effects, which are of course much easier to avoid in computational than in experimental studies especially if the matrix is composed of the same type of particles as the confined liquid (Figure 11a). Through calculations of position resolved correlation times (Figure 11b), it then appears that the dynamics of water strongly depends on the nature of the confinement wall. It is in particular about 100 times slower in the immediate vicinity of pinned water molecules than at larger distances even though peculiar attractive liquid–matrix interactions are absent [25].

A *dynamic length* ξ_d can in addition be obtained from an analysis of the distance up to which the dynamics of unpinned molecules is perturbed by their pinned counterparts. For water, one finds in this way that ξ_d increases by roughly a factor of 2 when the temperature decreases from 300 to 200 K [25]. The *static length* ξ_s also derived from neutral confinement conditions [25, 26] is a characteristic length up to which the positions of pinned and unpinned particles are substantially correlated. Comparing the

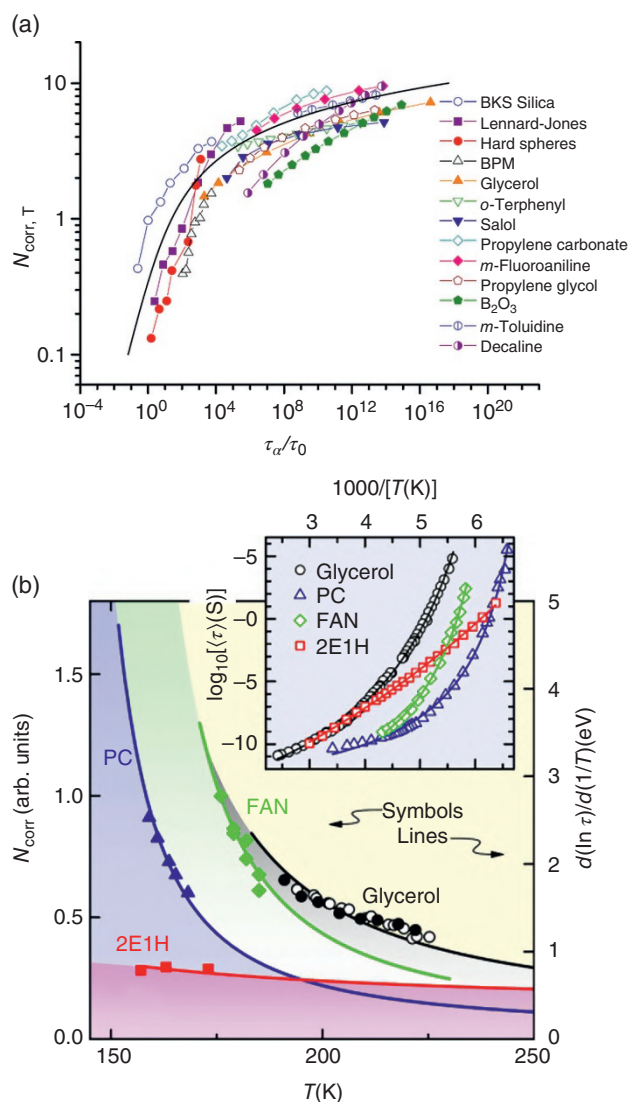


Figure 10 Number of dynamically correlated molecules in various glass-forming liquids as a function of temperature. (a) Data extracted from estimates of $\chi_4(t)$ and plotted against τ_α/τ_0 where τ_0 is a microscopic timescale. Black continuous line: crossover from a power law to a logarithmic growth upon cooling. Source: Reprinted with permission from Ref. [22]. Copyright 2007 APS Publishing. (b) Comparison of $N_{\text{corr}}(T)$ (symbols) obtained from the nonlinear dielectric susceptibility $\chi_3(\omega)$ with the effective activation energy $E(T)$ (lines) calculated from the temperature dependence of the α -process in the inset. Source: Reprinted with permission from Ref. [23]. Copyright 2013 APS.

temperature dependences of the length scales ξ_d and ξ_s for a binary mixture of quasi-hard spheres [26], one finds that ξ_d exhibits a non-monotonic temperature evolution with a maximum near the critical temperature T_c of mode-coupling theory, whereas ξ_s steadily grows upon cooling. These contrasting trends are consistent with the random-first-order theory of the glass transition and suggest a crossover from *flow* to *hopping* motion near T_c [10].

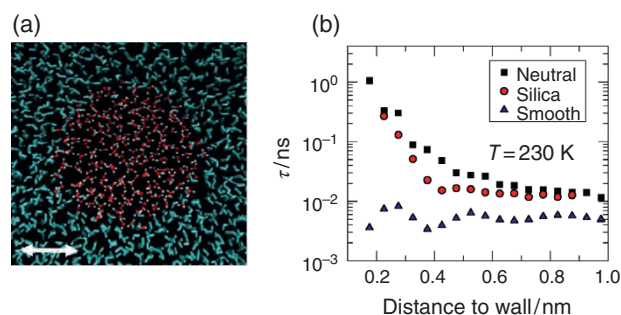


Figure 11 Molecular dynamics simulations of confined water. (a) Snapshot of water in a *neutral* environment of pinned water molecules at the center of the picture. (b) Correlation times for neutral dynamics as a function of the distances of the molecules to smooth [24], silica [24], and neutral walls [25].

3 Binary Glass-Forming Liquids

One-component molecular glass formers provide a valuable basis for the interpretation of the richer dynamical scenarios observed when different components are blended. Interest in multicomponent systems is to a great part triggered by their omnipresence in both everyday life and technological applications for which composition is often used to tailor material properties [27]. For such systems, however, a fundamental understanding is hampered by an overwhelming complexity, so approaches often focus on binary mixtures as simple model systems.

The outstanding dynamical properties of two-component systems are pronounced dynamical heterogeneities observed as broadened or even bimodal distributions of relaxation times that may be associated with violations of FTS [28, 29]. These heterogeneities have been explained in terms of local concentration variations that are either thermally driven or induced by the chain connectivity around one polymer segment.

Special attention has been paid to dynamically very asymmetric mixtures where additional effects come into play. Such mixtures are characterized by a high- T_g contrast between the individual components, which remain entirely miscible in spite of their strong dynamical decoupling. When undergoing isotropic reorientation far below the glass transition of the larger molecule [30], the smaller species may in fact experience the confinement exerted by a rigid matrix akin to that of supercooled liquids within nanometric pores [31].

Macroscopic miscibility does not necessarily imply a unique glass transition. Two transitions have been reported instead in miscible polymer blends and polymer-plasticizer systems as well as in mixtures of small organic molecules. A good example is that of 2-methyltetrahydrofuran ($C_5H_8O_2$) mixed with polystyrene (Chapter 8.8) of different molecular masses

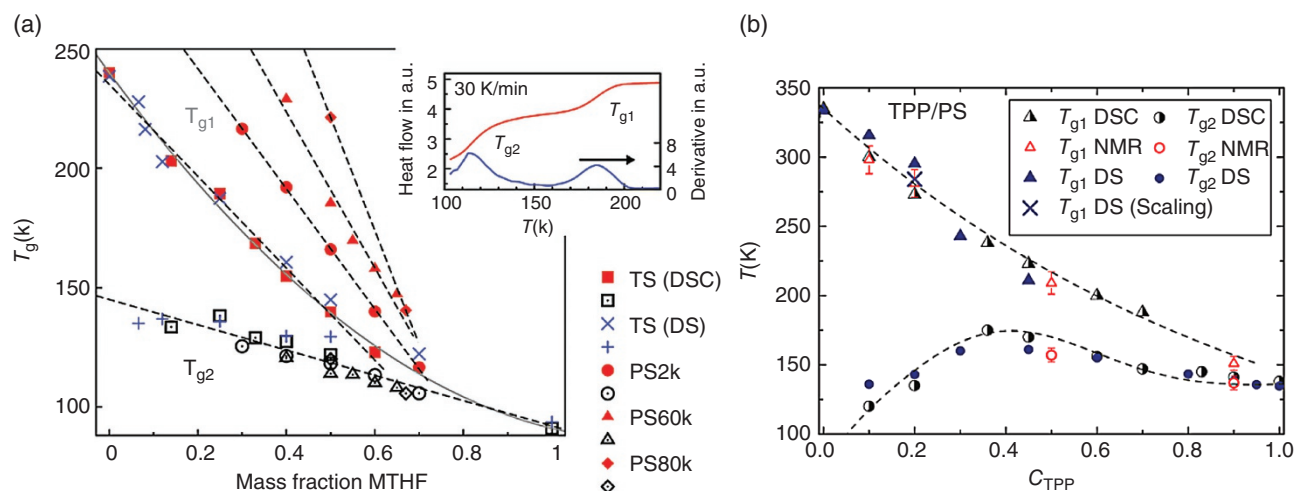


Figure 12 Double glass transition in binary mixtures. (a) 2-Methyltetrahydrofuran in polystyrene (PS) as observed by dielectric spectroscopy (DS) (crosses) and differential scanning calorimetry (other data) for the molar masses indicated (g/mol, TS: trimer). Inset: determination of the two T_g s from the DSC heat flow and its temperature derivative. *Source:* Reprinted with permission from Ref. [32]. Copyright 2012 AIP Publishing. (b) Tripropyl phosphate (TPP) in polystyrene (2 kg/mol): T_g as a function of concentration (mass percent) determined by DSC, DS, and NMR. *Source:* Reprinted with permission from Ref. [30]. Copyright 2014 AIP Publishing.

[32]. While the higher T_g strongly varies with composition and turns out to represent the α -relaxation of the matrix, the lower T_g changes much less as a result of the decoupling of the intrinsic α -relaxation of the small molecules (Figure 12a). Similar features are observed for tripropyl phosphate [$C_9H_{21}O_4P$] (Figure 12b), with the difference that the lower T_g displays a maximum at an intermediate concentration [30].

In accordance with the observation of two T_g , two different relaxation processes are observed in the dielectric spectra of binary mixtures (Figure 13). For the considered examples, DS essentially probes the relaxation of the small molecules due to strongly different dipole moments of the components. As is common in one-component glass formers, FTS holds reasonably well for the slower α_1 -relaxation, which is related to small molecules coupling to the matrix dynamics in spite of some peak broadening compared with the neat liquid (Figure 13b). By contrast, for the decoupled small molecules, pronounced FTS violations are observed (Figure 13c). In particular, the broadening observed on the low-frequency side of the peak caused by the presence of rigid walls is similar to that observed for supercooled liquids confined in nanoporous media [31].

At first glance, relaxation faster than the slowest α -process might be considered as secondary as it often shows Arrhenius temperature dependence. However, it turns out that the α_2 -process is associated with the second T_g in calorimetry (Figure 12). As indicated by NMR spectra, it involves isotropic reorientation of the smaller component in the frozen matrix [30]. Consistently, further

component-selective experiments show that the small molecules are associated with both α -relaxations (Figure 14).

As an example, Figure 14a shows the motion of 2-methyltetrahydrofuran, which can be selectively probed in a mixture with polystyrene 60k, by selective deuteration with QENS and due to the permanent dipole moment by DS. It then appears that the temperature dependence of the fast relaxation of the small molecules, which are embedded in an largely immobilized matrix of large molecules, changes from non-Arrhenian to Arrhenian below T_{g1} (Figure 14b), a so-called fragile-to-strong crossover, which is also observed in nanopore confinement experiments [31]. In addition, the small molecules take part in the slower α_1 -relaxation only below a certain temperature T_c . Above it, they relax without any coupling with the dynamics of the matrix. Below T_c , a fraction of the small molecules can only relax together with the α -process of the matrix [30, 32]. Interestingly, such a dynamic decoupling of large and small particles is predicted by MCT if the components differ sufficiently in size [33], in which cases the calculated correlation functions resemble that of Figure 14a. For quenched-annealed systems, this theory [34] in particular predicts higher-order singularities in the vicinity of which the correlation functions of the smaller molecules become particularly broad, e.g. quasi-logarithmic, consistent with the results of both simulations and experiments [35].

In conclusion, decoupling between the component dynamics in binary systems results in dynamical heterogeneities such that the α_1 -relaxation of large molecules

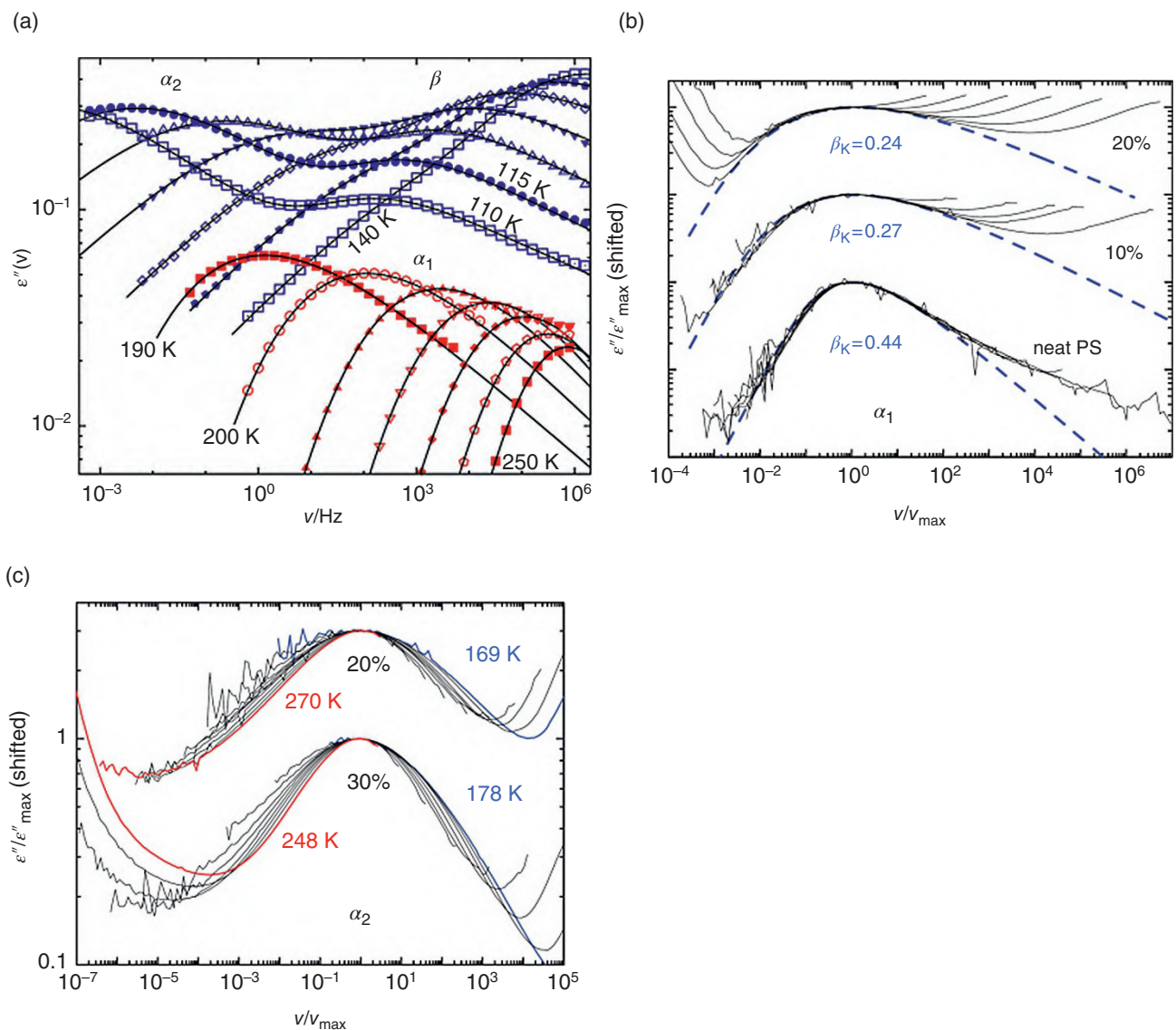


Figure 13 Dielectric relaxation of small molecules in dynamically asymmetric binary mixtures. (a) Dielectric spectra of 50 wt % 2-methyltetrahydrofuran in polystyrene (60k) at the temperatures indicated: fast β -relaxation and α -processes coupling (α_1) with or decoupling (α_2) from the matrix relaxation. *Source:* Reprinted with permission from Ref. [32]. Copyright 2012 APS. (b) and (c) Molecular reorientation of tripropyl phosphate in neat 2k polystyrene. Curves scaled to coincide at the position and height of the relaxation maximum. *Source:* Reprinted with permission from Ref. [29]. Copyright 2014 AIP Publishing.

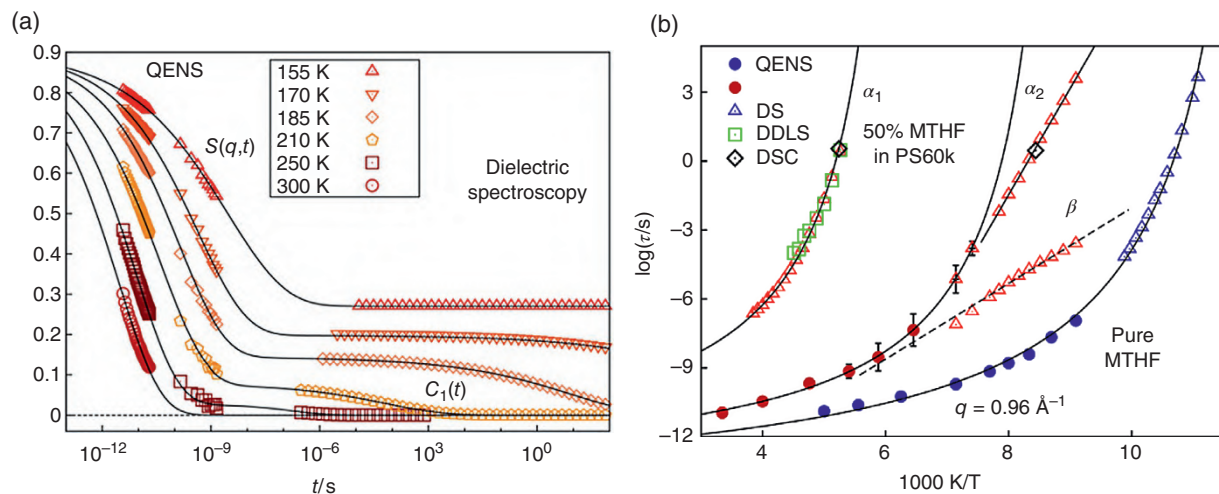


Figure 14 Dynamics of 2-methyltetrahydrofuran either pure or in a mixture with polystyrene (60k) probed by quasi-elastic neutron scattering and dielectric spectroscopy. (a) Self-intermediate scattering function $S(q, t)$ of the protonated species in a fully deuterated matrix and reorientational correlation function obtained from Fourier transformation of the DS spectra. (b) Time constants obtained by both methods. *Source:* Reprinted with permission from Ref. [32]. Copyright 2012 APS.

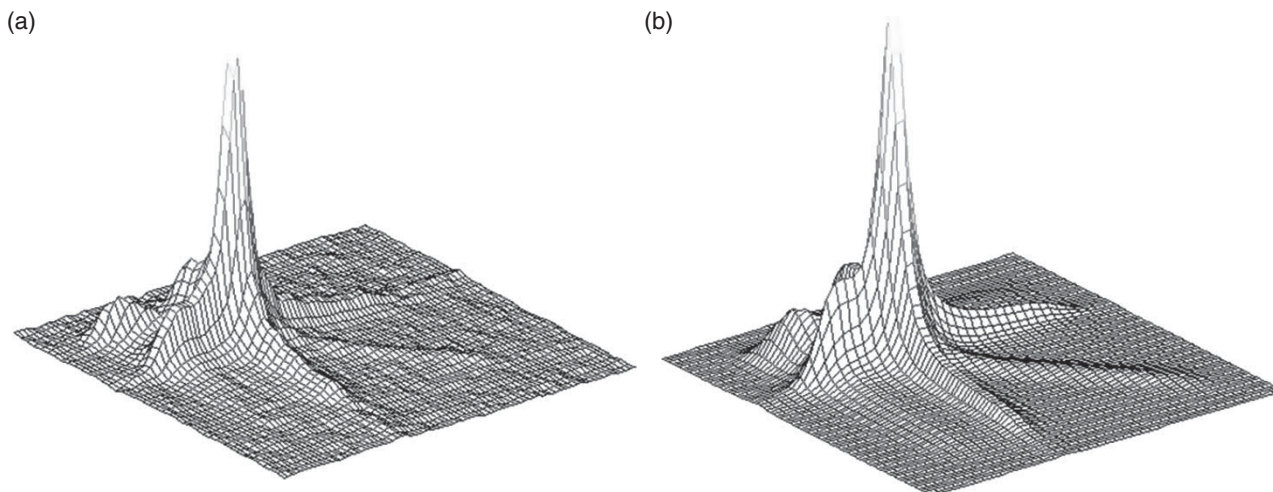


Figure 15 Indication of pronounced dynamic heterogeneities in binary glass formers. Cross-like pattern of a 2-D ^{31}P NMR spectrum of tripropyl phosphate in a mixture with polystyrene (2k) pointing to an exchange of correlation times between slow and fast molecules on the timescale of a mixing time $t_m = 1$ seconds. (a) Experimental spectrum at 269.5 K. (b) Model calculation of the spectrum using a two-phase model. Source: Reprinted with permission from Ref. [30]. Copyright 2014 AIP Publishing.

remains rather similar to that of neat glass formers, whereas the α_2 -process of small molecules is characterized by a strong broadening of the corresponding distribution $G_{\alpha 2}(\ln \tau_{\alpha 2})$, which may lead to the aforementioned quasi-logarithmic decays at low concentration. Even below T_{g1} , dynamic exchange occurs within $G_{\alpha 2}(\ln \tau_{\alpha 2})$, so fast molecules become slow and vice versa at a certain timescale. As illustrated by tripropyl phosphate (Figure 15), this exchange can be monitored by 2-D NMR spectroscopy whereby a cross-like pattern points to an exchange of correlation times between slow and fast molecules below 280 K, *slow* and *fast* referring here to

timescales longer and shorter than 10^{-5} seconds, respectively [30].

4 Secondary Relaxations

In addition to the α -processes, molecular systems show further relaxation features at higher frequencies such as the aforementioned excess wings, which emerge when approaching T_g [13, 17]. As an example (Figure 16a), DS measurements for sorbitol [$\text{C}_6\text{H}_{14}\text{O}_6$] show a pronounced β -relaxation peak that persists below T_g

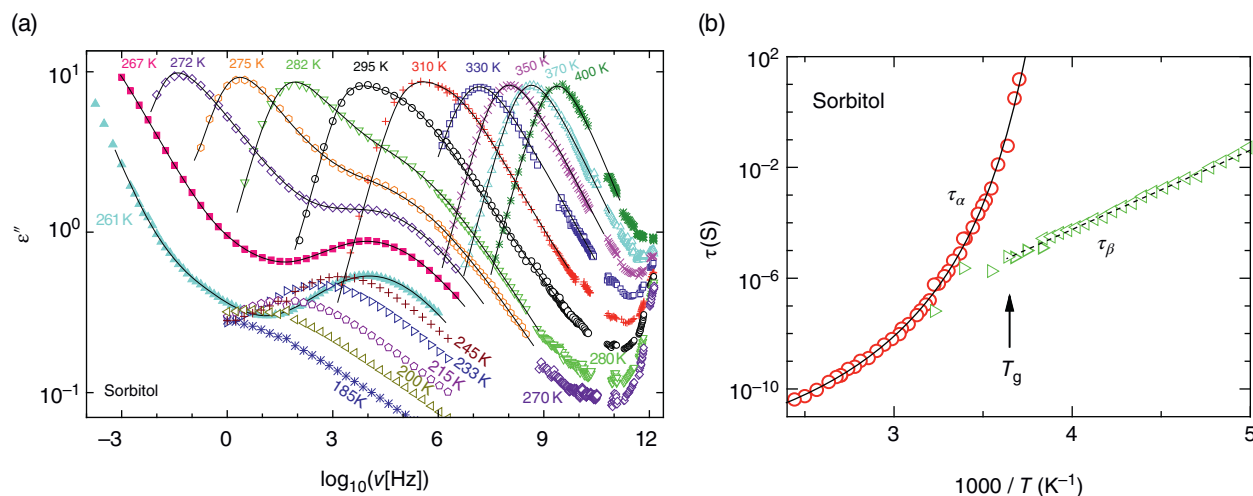


Figure 16 Double relaxation of sorbitol: α - and β -process. (a) Evidence from dielectric spectra. (b) High-temperature merging of the two relaxation peaks shown by the convergence of their associated time constants. Source: Reprinted with permission from Ref. [36]. Copyright 2007 IOP Publishing.

[36]. In many cases, the β - and α -processes merge at high temperatures, leaving the single α -relaxation displayed by sorbitol (Figure 16b). At $T < T_g$, its mean logarithmic correlation time τ_β follows an Arrhenius law with an activation energy $\langle E_\beta \rangle = 10\text{--}30 RT_g$, whereas its spectrum broadens with decreasing temperatures.

Secondary relaxation processes are observed in ionic and metallic glasses and in glasses of rigid molecules like toluene [13], indicating that they do not rely on intramolecular degrees of freedom. In some cases, both a β -relaxation and an excess wing are observed. Further relaxation features related to the low-temperature anomalies of glasses dominate at cryogenic temperatures but will not be discussed here.

Attempts have been made at classifying secondary processes [17]. For instance, it has been stated that the excess wing is a hidden β -process, which may separate from the α -peak under pressure or physical aging. In another group, JG β -relaxation exhibits a high sensitivity to pressure and is regarded as a genuine feature related to α -relaxation although its origin first remains unclear. Other secondary relaxations that do not fit in this scheme were interpreted to be of a *local* nature. However, molecules can only move in a concerted way in an isostructural state ($T < T_g$), thus the β -relaxation is likely not of local origin. Exceptions are symmetry-controlled motions such as rotation of methyl groups. Early attempts postulated *islands of mobility* representing some defects in the glass structure [37]. Yet, as demonstrated by NMR [38] studies, essentially all molecules participate in the JG β -process whose dynamics can be described by spatially highly hindered reorientation. Recent findings for binary glasses, however, suggest that this statement might not generally hold true [39].

The major features of separate β -peaks at ambient pressure displayed by viscous liquids can be summarized most conveniently based on DS results. With decreasing temperatures, one can map the spectral broadening of the JG β -relaxation onto a temperature-independent distribution of activation energies $g(E)$ [13]. Regarding the relaxation strength, it is nearly constant below T_g , but it begins to increase strongly upon heating through T_g , reflecting the *softening* of the material above the glass transition. Actually NMR results indicate that the extent of spatial restrictions during the JG β -relaxation is reduced above T_g [38].

The JG β -process of several glass-forming liquids as well as of glassy crystals has been investigated by ^2H and ^{31}P NMR with two-pulse echo sequences [38, 39]. Owing to its high sensitivity to small-angle reorientations, this technique yields a clear picture of the nature of the β -process. For several systems including plastic crystals (Figure 17), the NMR spectra show very similar line-shape changes. The exception is glycerol, which does not display a well-resolved β -process (Figure 1a). Specifically, when increasing the delay between the pulses, a decrease of the spectral intensity around zero frequency is observed if the pulse delay is similar to the correlation time τ_β . One can reproduce well the spectra by taking recourse to a wobbling-on-a-cone model with a cone angle lower than 10° . Investigations of the β -process in mixed glasses have shown that the different components participate in the β -process independently of their shape and size [38]. For polymer-plasticizer systems, both the polymer chains and the plasticizer molecules participate in the β -relaxation, pointing to a cooperative nature of the β -process [39]. Finally, we note that the β -process is also probed by DLS, although its appearance in DLS may depend on details of the molecular structure (Figure 18) [16, 40].

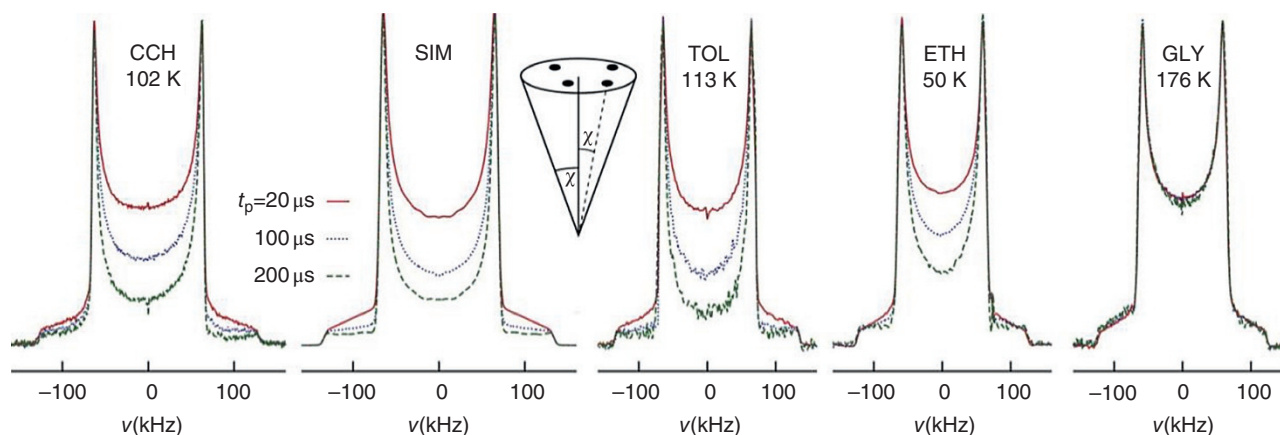


Figure 17 Johari–Goldstein relaxation observed in ^2H NMR solid-echo spectra for different pulse delay t_p for cyanocyclohexane plastic crystal (CCH) and toluene (TOL), ethanol (ETH), and glycerol (GLY) glasses. Spatially highly hindered motion of essentially all molecules allows one to simulate (SIM) in the spectral changes with increasing t_p [38].

5 Plastic and Glassy Crystals

Calorimetric and dielectric studies were also among the first to show that certain crystals exhibit features well known in supercooled liquids [41]. Because dielectric spectra probe the reorientation of dipolar molecules, which may persist in the crystal, such molecular rotation becomes sufficiently slow to be arrested below some temperature, provided that a transition to a rotationally ordered phase does not occur. Indeed, the calorimetric signature of a glass transition is found, indicating, by analogy with supercooled liquids, that cooperative molecular reorientation becomes too slow to be observed at the timescale of the experiment. Moreover, the non-Arrhenius temperature dependence of the main (α -) relaxation is revealed and even β -processes are observed as shown by cyanocyclohexane (Figure 18a) [42]. Such crystals with cooperative rotational dynamics must be

distinguished from the so-called rotor phases like crystalline benzene where the molecular reorientation reflects a high symmetry of the molecule and cooperativity is not involved. Below T_g , the centers of the molecules form a three-dimensional lattice (often of cubic symmetry), but their orientations are arrested in a more or less random fashion, which is why the term *glassy crystal* has been coined.

Many plastic crystals have been studied [43]. A prominent example is ethanol, which forms a metastable plastic crystal upon sufficient supercooling (Figure 18b) [44]. In spite of somewhat different fragilities, this crystal and the liquid have the same $T_g = 98$ K. Most intriguingly, the dielectric spectra of both phases are almost indistinguishable (Figure 18b): a strong main (α -) process, a β -process with its Arrhenian time constant $\tau_\beta(T)$, and even traces of an excess wing are recognized. Most importantly, the NMR signature of the β -process

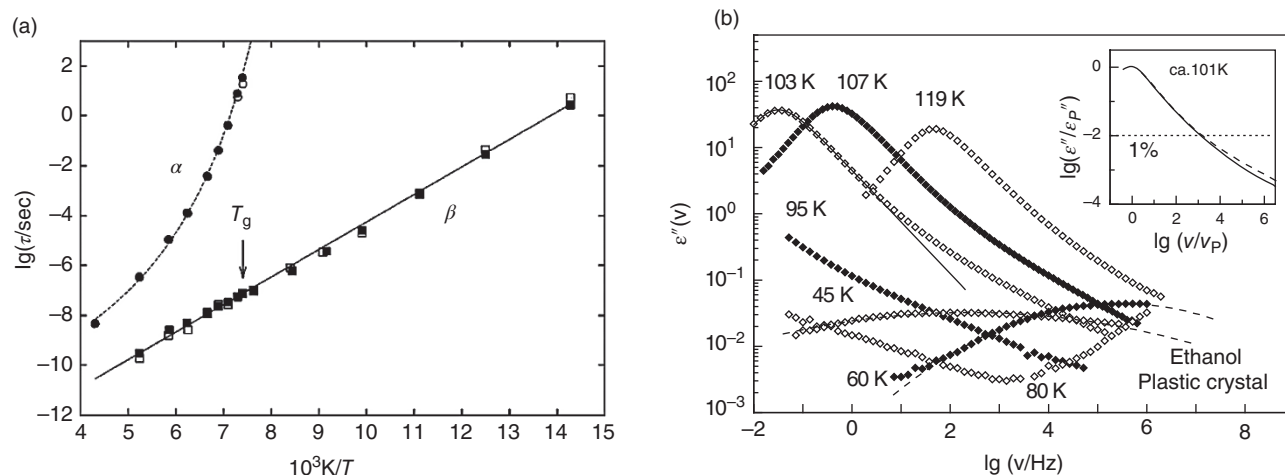


Figure 18 Relaxation in plastic crystals. (a) Time constants of the α - and β -process in cyanocyclohexane revealed by DS. Source: Reprinted with permission from Ref. [42]. Copyright 2012 AIP Publishing. (b) Dielectric spectra of ethanol. Inset: α -relaxation in the crystal (dashed lines) and liquid phases (solid line). Source: Reprinted with permission from Ref. [44]. Copyright 1998 IOP Publishing.

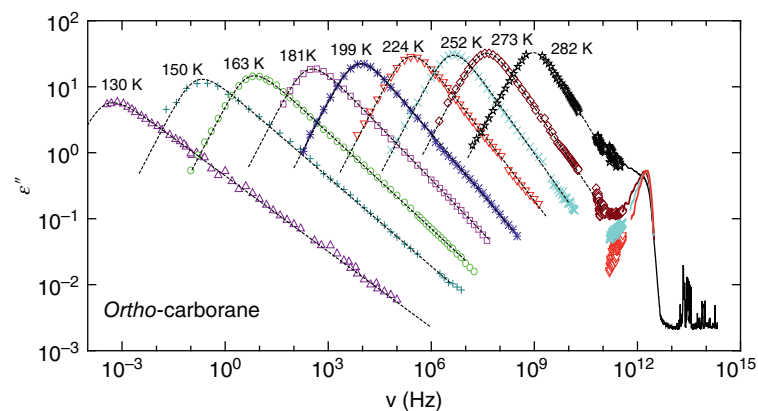


Figure 19 Lack of secondary relaxation apparent in broadband dielectric spectra of *o*-carborane plastic crystal above its T_g of about 130 K including the IR band. Source: Reprinted with permission from Ref. [45]. Copyright 2006 IOP Publishing.

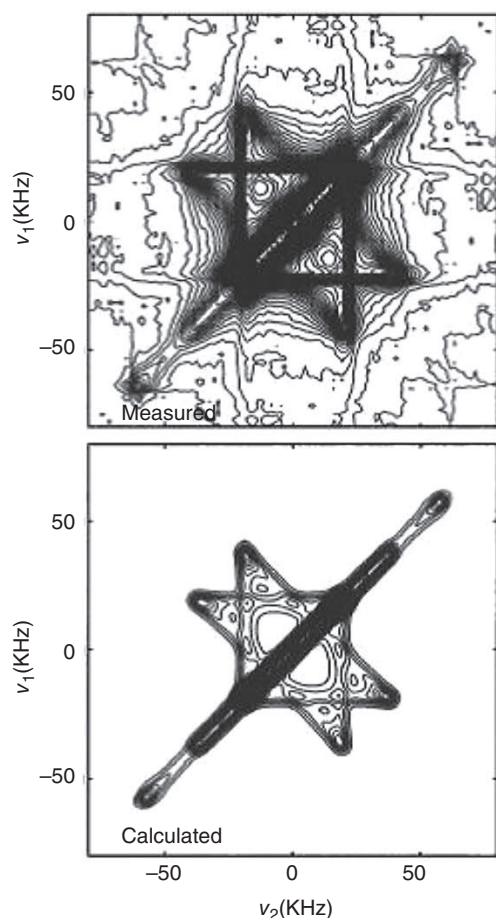


Figure 20 The 90° jumps of cyanoadamantane molecules in the plastic crystal phase clearly visible in the observed and calculated 2-D ^2H NMR exchange spectrum. *Source:* Reprinted with permission from Ref. [46]. Copyright AIP Publishing.

cannot be distinguished from that of a β -process in molecular liquids (Figure 17). Thus, spatially highly restricted reorientations are involved, too.

Somewhat different DS spectra (Figure 19) are found for o-carborane [$\text{C}_2\text{B}_{10}\text{H}_{12}$] [45]. In this case, the main relaxation strongly broadens upon cooling, so FTS does not apply and the spectra can be fully described by Cole–Davidson functions, i.e. no secondary relaxation emerges above T_g . For the plastic phase of cyanoadamantane [$\text{C}_{10}\text{H}_{15}\text{CN}$], 2-D ^2H NMR shows that the reorientation takes place via jumps of 90° determined by the cubic structure of the lattice; no free isotropic rotation occurs close to T_g (Figure 20) [46].

6 Perspectives

From high temperatures down to the glass transition, significant progress has recently been achieved in elucidating

the generic dynamics of molecular liquids at timescales ranging from picoseconds to seconds. This progress has been made possible by improved experimental techniques, which are increasingly able to cover the full frequency and temperature ranges with high precision. Yet, many aspects, although quite universally observed in many types of molecules, remain poorly understood. First of all, there is still no generally accepted theory of the glass transition. Aside from further ongoing developments of MCT, ideas related to the random-first-order transition theory have recently received a considerable attention as simulations and dedicated experiments have shed new light on the time-honored topic of growing length scales upon supercooling. At the same time, supercooled liquids are investigated in increasingly complex environments, such as multicomponent systems or nanoscale confinement, that are relevant to biology or technological applications. Because dynamic scenarios are even more complicated in such contexts, theoretical advances are badly needed to remedy the currently rather rudimentary state of understanding of these phenomena.

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8.7

Physics of Polymer Glasses

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1 Introduction

Known since the early use of the milky latex of the rubber tree (*Hevea brasiliensis*), polymeric matter was first synthesized in 1870 as a substitute for ivory in the form of celluloid by reaction of nitrocellulose $[\text{C}_6\text{H}_7(\text{NO}_2)_3\text{O}_5]$ with camphor $[\text{C}_{10}\text{H}_{16}\text{O}]$. Usually, however, one rather assigns to 1909 the birth of the *plastics era* with the invention in the US of bakelite $[(\text{C}_6\text{H}_6\text{O}\cdot\text{CH}_2\text{O})_n]$ by the Belgian-born chemist Leo Baekeland because this new material formed through polycondensation of phenol $[\text{C}_6\text{H}_6\text{O}]$ with formaldehyde $[\text{CH}_2\text{O}]$ quickly found many applications thanks to its electrically insulating and heat-resistant properties. Since then, several hundreds of organic macromolecules have been synthesized, and the world production of plastics has reached 335×10^6 tons in 2016. From food containers, insulating foams and films to prostheses, and complex optical components, plastics have become so ubiquitous in daily life that, despite their strongly technical nature, terms such as polystyrene, polyethylene, polypropylene, polyurethane, and even polycarbonate are now household names (Chapter 8.8).

That these materials are basically glassy is highlighted by the name *Plexiglas* commercially given to methyl polymethacrylate when it was introduced on the market in 1933. This glassy character lies at the root of most uses of plastics as these materials can be shaped into any form, like oxide glasses, but more readily so in view of glass transitions occurring at temperatures always lower than

500 K. Because most plastics are primarily made up of the light elements C, H, O, and N, they have the important advantage of a low density of only $\sim 10^3 \text{ kg/m}^3$ combined with a definite resistance to breakage and a good chemical inertness. Finally, although they suffer from being combustible materials, their strength can be improved through partial crystallization or incorporation of mineral particles.

Plastics owe their fundamental importance to the nature of their macromolecular elements. All of them represent a sequence of a number as large as 10^4 of concatenated identical monomeric units that form a chain, whence the common prefix *poly* they share. Each macromolecule may be represented as a hairlike filament at a scale much smaller than $1 \mu\text{m}$. The main question dealt with in this chapter is how such a microscopic feature translates into the bulk plastic properties that make these amorphous organic materials so valuable.

For this purpose, attention will be first paid to the characteristic elasticity of a macromolecule in the liquid state, which results from the flexible concatenation of units subjected to a mechanism of rotational isomerization. We will then focus on the concept of fractional free volume as applied to the interpretation of the temperature dependence of viscoelastic response of polymeric liquids. This response is associated with a hierarchy of relaxation rates, which govern the segmental rearrangements of chains associated with the glass transition. Their signature will be discussed with respect to a variety of physical properties. Attention will also be paid to local chain rearrangements that give rise to secondary transitions below the glass transition region. Finally, the influence of partial crystallization and addition of mineral particles on polymer properties will be briefly discussed, and some applications of polymer science to films, fibers, foams, hollow fibers, and porous membranes will be described.

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2 Polymeric Chains

2.1 Polymer Macromolecules

In preamble, some fundamental properties of the constituents of polymeric liquids must be described. As already stated, any polymeric material is made up of macromolecules formed from long sequences of concatenated identical monomer units linked to one another by covalent bonds, which define the skeleton of each molecule; for example, $-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-$ and $-\text{O}-\text{Si}(\text{CH}_3)_2-$ chemical groups are the monomer units of polystyrene and silicone chains, respectively. The synthesized macromolecules may comprise a number N of monomeric units as large as 10 000 so that the length of a fully extended chain skeleton may be of the order of $1\ \mu\text{m}$, whereas its diameter may be as small as half a nanometer. The very high ratio between the length of a polymer chain and its mean diameter is a feature analogous to that of a hair; it underlies all characteristic properties of polymeric matter.

2.2 Skeletal Bond Rotations

Chain skeletons are usually successions of carbon ($-\text{C}-\text{C}-$) or oxygen and silicon atoms ($-\text{Si}-\text{O}-$, in silicone); in most descriptions of the physical properties of macromolecules, bond lengths are considered as fixed and angles between any two successive bonds supposed to be constant. In molten polymers or in polymer solutions, each skeletal bond within a macromolecule can rotate about the axis defined by its preceding bond, so two angles per bond are required to specify the conformation of one chain in space. We will thus denote by θ the angle between two successive bonds and by ϕ the angle of rotation of one bond about its preceding one. Such bond rotations are a fundamental feature because they cause chains to be highly flexible and polymers to be highly elastic at a macroscopic scale. For polystyrene, a schematic representation of a succession of three ($-\text{C}-\text{C}-$) bonds, with phenyl groups and hydrogen atoms attached to the skeleton, is shown in Figure 1.

Owing to the very large number of its internal degrees of freedom, each macromolecule is considered as a physical system as a whole in the sense that usual thermodynamic functions (entropy, internal energy, free energy) can be applied to describe its properties within the framework of statistical physics. But it must be emphasized that the presence of side chemical groups bound to the chain skeleton, like methyl groups in silicones, for example, hinders internal rotations of monomeric units so that interactions between contiguous side groups give rise to an internal cooperative behavior along each macromolecule.

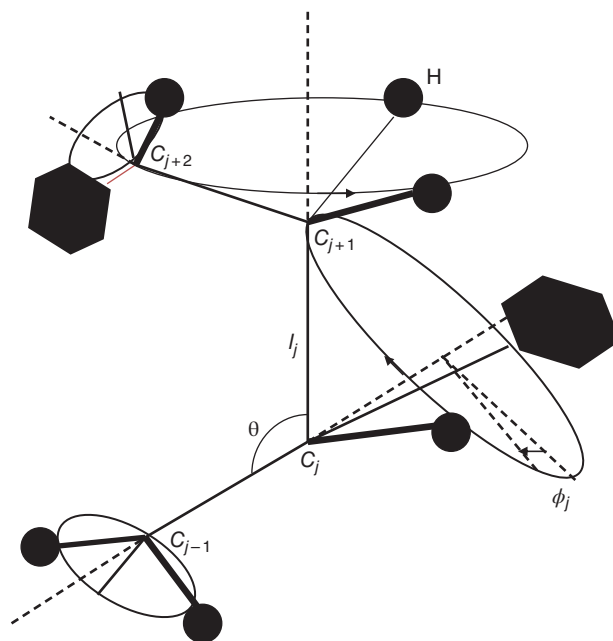


Figure 1 Schematic representation of the succession of three ($-\text{C}-\text{C}-$) skeletal bonds with phenyl groups and hydrogen atoms (H) attached to the chain.

2.3 Chain Stiffness

The interdependence of bond rotations determines chain stiffness as quantified by the *characteristic ratio* C_∞ , which is defined as the limit, for long chains, of the ratio of the mean square distance between the ends of a macromolecule $\langle R^2 \rangle$ and the sum of square lengths of skeletal bonds. If one assumes that each skeletal bond is defined from a vector $\mathbf{l}_j$, the end-to-end vector $\mathbf{R}$ is the sum over bond vectors:

$$\mathbf{R} = \sum_j^n \mathbf{l}_j, \quad (1)$$

where n is the total number of skeletal bonds in one chain. The mean square end-to-end distance then reads

$$\langle R^2 \rangle = \left\langle \sum_j^n \mathbf{l}_j^2 + \sum_j^n \sum_{j \neq k}^n \mathbf{l}_j \mathbf{l}_k \right\rangle. \quad (2)$$

In the case of equal bond lengths, the characteristic ratio is expressed as

$$C_\infty = 1 + \frac{1}{nl^2} \left\langle \sum_j^n \sum_{j \neq k}^n \mathbf{l}_j \mathbf{l}_k \right\rangle. \quad (3)$$

The second term on the right-hand side of Eq. (3) accounts for the effect of interrelated rotations of skeletal bonds in real chains. If hindrance to bond rotations is neglected, the characteristic ratio C_∞ is expressed as

$(1 + \cos(\pi - \theta))/(1 - \cos(\pi - \theta))$ whose value is thus 2 for tetrahedrally bonded chains ($\theta = 109^\circ 28'$). In real chains, the deviation from this value reflects the extension of correlations of bond vector orientations with respect to a given skeletal bond: the memory of correlations of bond orientations spreads over a chain segment length equal to lC_∞ on average. All studied chains exhibit a characteristic ratio higher than 4, the experimental values of C_∞ lying in the 4.0–10.0 range as shown by data summarized for real chains [1, 2].

The mean square end-to-end distance $\langle R^2 \rangle$ is conveniently measured from light scattering and/or viscosity experiments performed on ideal and dilute polymer solutions [3]. Ideal conditions are realized within short concentration and temperature ranges specific to a given polymer/solvent mixture; these conditions are obtained when the excluded volume effect resulting from interactions between pair of monomer units and solvent molecules cancels out. Correspondingly, the distribution of units in space obeys Gaussian statistics for long flexible chains. Light scattering experiments require that average chain sizes be comparable to the wavelength of light. Both types of experiments provide numerical values of $\langle R^2 \rangle$: the chain stiffness can be then quantified from the ratio $\langle R^2 \rangle m_u / M l^2$, where M is the chain molecular weight, whereas m_u is the mean molecular weight per skeletal bond.

2.4 Rotational Isomers

Potential energies of steric repulsion between atoms and chemical groups attached to neighboring units hinder the internal rotations of skeletal bonds; these energies strongly depend on the distances between all atoms along a given chain. The averaging of physical properties over all conformations possibly achieved by a chain then depends on the sum of these potential energies; consequently, skeletal bonds cannot be considered as statistically independent from one another within the framework of statistical physics. Every chain is in fact analogous to a one-dimensional cooperative system [4].

A rigorous theory is lacking to calculate macromolecular averages of physical quantities from the interaction energies of all the units considered. Fortunately, however, one can overcome this difficulty with the assumption that the rotation of a skeletal bond is not a continuous process in space but is governed by the existence of discrete rotational isomeric states. This assumption is similar to that made when deriving the properties of internal bond rotations from microwave spectroscopy investigations of rotational bands. For simple molecules such as gaseous ethane, these studies have shown that the internal bond rotation is related to a continuous potential energy

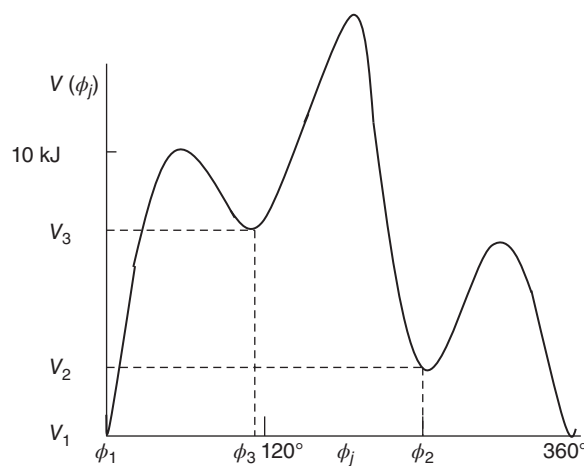


Figure 2 Schematic representation of the mean potential energy of rotation of one skeletal bond about its preceding bond considered as an axis.

function exhibiting minima and energy barriers usually higher than the room-temperature thermal energy [1].

For the sake of simplicity, we show in Figure 2 a schematic representation of the mean potential energy of rotation of one skeletal bond labeled j , which takes into consideration the influence of close neighboring bonds. But such continuous values cannot be introduced as a whole within the framework of statistical physics applied to the description of macromolecular properties. One assumes instead that all potential minima V_1 , V_2 , and V_3 can be assigned to an equilibrium isomeric state of bond rotation; in other words, each energy minimum characterizes a rotational isomer such that the angle variable ϕ is given the discrete values ϕ_1 , ϕ_2 , and ϕ_3 that characterize the minima of Figure 2. Any macromolecular conformation represents successive transitions in space from an isomeric state of one bond to another state of a contiguous bond; a temperature-dependent statistical weight determined from the energies of the corresponding minima thus is assigned to each chain conformation. In this way the rotational isomeric structure of linear macromolecules underlies all physical approaches to the descriptions of the properties of polymeric matter.

3 Polymeric Liquids

3.1 The Basic Importance of Viscoelasticity

A fundamental feature of any polymeric liquid is the elasticity induced by the collective nature of random internal chain motions, which is superimposed on viscous deformation. In the liquid state all chains have the form of coils

that unfold into one another. The transitions of skeletal bonds from some isomeric states to others require jumps over potential energy barriers that occur with temperature-dependent probabilities per unit time. These jumps cause large conformational fluctuations of chains, which make macromolecules essentially entropic systems. The resulting distributions of distances between the ends of any segment and between chain ends are Gaussian regardless of chain length, provided the number of skeletal bonds n is higher than about 20. Because these fluctuations cause a very large array of conformations to be explored per unit time, they induce diffusive motions of translation and rotation of the macromolecules that are characterized by a temperature-dependent correlation time, τ_R .

At about 100 K above the glass transition, a skeletal bond jump occurs every 10^{-9} seconds on average within polymer chains in the liquid state; this time interval is sensitive to restrictions of local volume around skeletal bonds and strongly depends on temperature. For short chains, τ_R is proportional to the number N of units according to Rouse model of internal random chain motions [5]. For polystyrene, with N equal to 35, τ_R is of the order of 10^{-4} seconds about 100 K above the glass transition. More precisely, conformational fluctuations of segments belonging to a chain obey a hierarchy of time-scales: the longer the segments the longer the relaxation times that govern their fluctuations. The limit to these relaxation times is the terminal relaxation time τ_R , associated with the random motions of a chain considered as a whole.

3.2 The Fractional Free Volume

At the nanometer scale volume constraints manifest themselves by friction effects that affect all dynamical properties of polymers even at a macroscopic scale. For each bond, random rotation requires an appropriate local volume to be generated by the rotations of the surrounding units under the influence of thermal energy at temperature T . The concept of fractional free volume has been introduced to account for the shrinkage of this local volume when the polymer temperature, and consequently its thermal energy, is lowered. For this purpose, the specific volume of a polymeric liquid v is considered as the sum of two terms: the first, v_0 , corresponds to the molecular volume defined by electronic orbitals and van der Waals interactions, whereas the second is the free volume $v_f = v - v_0$, which vanishes at the glass transition. The *fractional free volume* is then defined as the ratio $f = v_f/v_0$. The relaxation times associated with volume restrictions and friction effects on bond mobility, and consequently all macromolecular internal relaxation processes, are

proportional to a monomer friction coefficient, ζ_0 , which can be expressed as a function of f as [5]

$$\zeta_0 = \exp\left(\frac{B}{f}\right), \quad (4)$$

This expression was established by Cohen and Turnbull [6]. It is based on the general assumption that any molecule is able to move whenever a free space exceeding a critical volume is created in its immediate vicinity, which is why the coefficient B is of the order of unity. The dependence of f on temperature obeys the linear equation

$$f(T, T_0) = f_0(T_0) + \alpha_f(T - T_0), \quad (5)$$

where $f_0(T_0)$ is the free volume fraction at the chosen reference temperature T_0 and α_f is the coefficient of thermal expansion of the free volume, which is of the order of $3 \times 10^{-4} \text{ K}^{-1}$; comparisons between friction coefficients $\zeta_0(T)$ and $\zeta_0(T_0)$ at temperatures T and T_0 are conveniently made in the form of the ratio $a(T, T_0)$:

$$a(T, T_0) = \frac{\zeta_0(T)}{\zeta_0(T_0)}, \quad (6)$$

or

$$\ln[a(T, T_0)] = - \frac{B(T - T_0)}{f_0(T_0)(T - T_0 + f_0(T_0)/\alpha_f)}. \quad (7)$$

The empirical Williams, Landel, and Ferry (WLF) equation,

$$\log[a(T, T_0)] = - \frac{C_1^0(T - T_0)}{(C_2^0 + T - T_0)}, \quad (8)$$

has been widely used before Eq. (7) was introduced. The coefficients of Eqs. (7) and (8) are related by $C_1^0 = B/(f_0 \ln[10])$ and $C_2^0 = f_0/\alpha_f$. By changing the reference temperature from T_0 to T_1 and combining Eqs. (5) and (7), one finds that the products $C_1^1 C_2^1$ and $C_1^0 C_2^0$ are equal, as well as the differences $T_0 - C_2^0$ and $T_1 - C_2^1$; the former, $T_\infty = T_0 - C_2^0$, is the well-known Vogel temperature (Chapter 4.1) where C_2^0 is of the order of 60 K for most polymers. Numerical values of f_0 and α_f have been tabulated for a large number of polymers; for example, the ratio f_0/B is of the order of 0.030 at the glass transition temperature for more than 30 commonly used polymers [5].

3.3 Viscoelastic Properties

As any liquid, polymer matter under stress flows viscoously via the random motion of its macromolecular components. In addition to this viscous response, the chain structure gives rise to an elastic response, observed

as well on dilute polymer solutions. Except in the glass transition range, such an effect is negligibly small in ordinary liquids where it lasts over 10^{-12} seconds or less, whereas it may last for several days or more in high-molecular-weight polymers. For polymeric liquids, one conveniently observes viscoelasticity by applying a sinusoidal strain characterized by a pulsation ω and a weak amplitude of deformation. The linear response to such a strain is a stress that consists of distinct elastic and viscous components: the former, in phase with the strain and accounting for elasticity, is characterized by the *storage* modulus $G'(\omega\zeta_0/T)$. The latter, 90° out of phase with the strain and accounting for viscous dissipation, is characterized by the *loss* modulus $G''(\omega\zeta_0/T)$. At low enough frequencies, i.e. when $\omega\tau_R < 1$, the amplitude of $G''(\omega\zeta_0/T)$ is much higher than that of $G'(\omega\zeta_0/T)$, whereas both moduli become nearly equal at higher frequencies where $\omega\tau_R > 1$. The ratio between the energies lost and stored during one cycle of strain defines the *loss tangent*, $\tan \delta(\omega) = G''(\omega\zeta_0/T)/G'(\omega\zeta_0/T)$, $\delta(\omega)$ being the loss angle.

The characteristic Eq. (7) leads to a remarkable method of analyzing the frequency–temperature dependence of $G'(\omega\zeta_0/T)$ and $G''(\omega\zeta_0/T)$ responses represented in log–log plots; according to the principle of corresponding states, performing measurements at the frequency ω_0 and at temperature T_0 is tantamount to making observations at the frequency ω' and temperature T' such that $G'[\omega_0\zeta_0(T_0)/T_0] = G'[\omega'\zeta_0(T')/T']$. Correspondingly, ω_0 and ω' frequencies obey the relationship: $\ln(\omega'/\omega_0) = \ln[a(T_0, T')T'/T_0]$; with the assumption that T_0 is higher than T' , then the friction coefficient $\zeta_0(T_0)$ is smaller than the friction coefficient $\zeta_0(T')$, and the ratio $a(T_0, T')T'/T_0$ is smaller than one. Consequently, the experimentally observed curve at temperature T' is shifted as a whole from that observed at temperature T_0 ; the shift toward lower frequencies is defined by the above ratio, applied along the logarithmic frequency scale. Notwithstanding the narrow range of frequencies that can be experimentally explored, this principle makes the determination of experimental values of $G'(\omega\zeta_0/T)$ and $G''(\omega\zeta_0/T)$ possible over a broad range, typically $1-10^8$ rad/s. For example, varying the polymer temperature from 260 to 400 K amounts to shifting the relevant frequency from 10 to 10^4 rad/s [5].

3.4 Temporary Elasticity

Contrary to short chains, long macromolecules in polymeric liquids are subjected to topological restraints. In the frequency spectrum, these induce a splitting of the storage modulus $G'(\omega\zeta_0)$ in two parts separated from each other by a *plateau modulus*, G_N^0 . In the frequency range of the plateau, $\Delta\omega_G$, the proportionality of the

stress to the strain represents an elasticity effect occurring over a time range of 10^{-3} to 1 seconds, which is roughly equal to $1/\Delta\omega_G$ and is characterized by a modulus G_N^0 of the order of 10^5 Pa for most polymers. The *plateau modulus* is interpreted as reflecting a delay that takes place during the stress polymer response to a sudden strain. About 100 K above the glass transition, at high frequencies of about 10^8 rad/s, $G'(\omega\zeta_0)$ and $G''(\omega\zeta_0)$ reflect short-range cooperative rotations of skeletal bonds, which are independent of chain length. At low frequencies of about 1 rad/s, both moduli are governed by a terminal relaxation time specific to long chains, τ_R , such that $\omega\tau_R < 1$.

This relaxation time τ_R is proportional to the local friction coefficient and follows a power law of the number N of units whose exponent is 3.4 (instead of unity for short chains). More precisely, long-range motions of long chains can be schematically depicted as if they were taking place in a tube built from topological restraints (Figure 3); diffusive linear motions of a whole chain within its tube have been described according to the reptation model, proposed by de Gennes [7, 8]. Importantly, these random motions are unrelated to local fluctuations of units that occur within the short segments made up of a characteristic number N_e of monomer units. Depending on the chemical nature of the polymer, N_e ranges from about 100 to 200. In other words, a screening of molecular weight effects takes place along these characteristic segments.

The frequency splitting of the storage modulus $G'(\omega\zeta_0)$ is specific to all high-molecular-weight polymers. Near the glass transition, the cooling rate of the polymer must be compared with the broad spectrum of rates of rearrangements of macromolecular conformations, closely

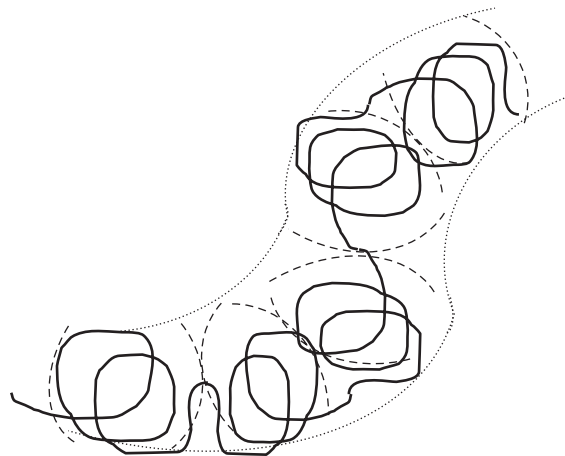


Figure 3 Mean effects of topological restraints exerted on a chain are schematically depicted as those of a tube (dotted curves) surrounding concatenated segments made up of a characteristic number N_e of monomer units (in between broken lines).

related to chain segment lengths; some relaxation modes characterized by rates shorter than the cooling rate of the polymer do not take place completely so that this truncating effect determines both the spread of the transition and the resulting glassy state.

4 Polymer Transformations

4.1 Partly Crystallized Polymers

Owing to topological restraints and stiffness, long flexible chains cannot completely order even upon slow cooling. In polymers, where crystallites are made up of helical segments arranged side by side, the degree of crystallinity does not exceed 90%, the highest value being reached for polypropylene [9]. Because any long chain may participate in the formation of several contiguous domains, crystallites are connected to one another by soft segments left out of ordered domains.

In most polymers, crystallites appear as lamellae with a 10–15 nm thickness and much broader transverse dimensions. Contrary to the precipitation of crystals in ordinary liquids, the formation of these crystallites necessitates displacements of monomer units to create the structures defined by adjacent helical segments. Helices occur in stereoregular segments built from identical repeating units attached to each other by successive head-to-tail covalent links. In contrast, helices do not form in concatenated segments comprising repeating units with a different chemical nature or built according to tail-to-tail or head-to-head links. This lack of stereoregularity and uniform chain tacticity then prevents crystallization from occurring at all.

As described for other glass-forming systems (Chapter 5.4), crystallization does not begin at the liquidus but below, because the positive interfacial energy of the crystallites must be balanced by their negative bulk free energy, which is an increasing function of the degree of supercooling. The rate of formation of ordered domains also depends on the degree of supercooling: it is equal to zero at the liquidus or at the glass transition and goes through a maximum at intermediate temperatures, hence the need of quenching polymers to prevent them from crystallizing before they undergo the glass transition. Besides, polymer crystallites are also organized on a large scale in the form of spherulites characterized by diameters of the order of 100 μm , which strongly improve mechanical properties. The usual opacity of crystalline polymers thus arises from the presence of these spherulites whose size is much larger than visible light wavelengths.

4.2 Gels

Another important transformation results from the creation of cross-links usually formed at random between long polymer chains from covalent bonds involving foreign

atoms (Chapter 8.8, [10–12]). The process gives rise to a network, called a gel, depicted as an ensemble of segments whose ends are fixed by these covalent cross-links, which prevent chains from flowing and ensures material elasticity instead. A case in point is the network formed by polybutadiene chains $(-\text{CH}_2-\text{HC}=\text{CH}-\text{CH}_2-)_n$ between which covalent bridges are made up of short chains of sulfur atoms. This is an example of the vulcanization process, which is at the roots of the rubber industry where a variety of catalyzing and curing agents are required to achieve optimal chain cross-linking.

As in a liquid, conformational changes of segments still occur, but their amplitudes are necessarily more restricted than those developing within segments in the melt; each segment nevertheless keeps its flexibility, ensuring the collective elasticity of the ensemble. When a gel reversibly undergoes a high deformation, an internal force of retraction exerts itself on the stretched network, but, as noted above, the presence of cross-links prevents the soft polymer from flowing.

5 Glass Transitions and Aging

5.1 α Glass Transition

Some polymers do not crystallize at all because of the strong irregularity of the way in which their monomer units are concatenated. When cooled at sufficiently low temperatures, however, all polymers undergo a glass transition that affects every segment of the network [13]. Contrasting with the macromolecular dynamics observed in the liquid state, no large amplitude random motions of chain segments then occur in the glassy state: skeletal bonds are subjected only to vibrations and torsional oscillations.

In any polymeric liquid there is in fact a hierarchy of timescales characterizing random internal motions of chain segments such that, in the broad spectrum of observed relaxation times, the longest relaxation times are associated with the longest chain segments. Upon cooling, the probabilities of rotational jumps over potential energy barriers strongly diminish, and the free volume, which is thermally activated, also decreases down to the glass transition where it is supposed to vanish. Correspondingly, the increase of the local friction coefficient causes internal chain relaxation times to become longer. The glass transition thus results from the progressive slowing down process of rearrangements of conformations occurring on cooling, whereby macromolecules explore a more and more restricted array of conformations during a given time interval.

According to the space–time hierarchy, which characterizes the internal fluctuations of chains, this process

first affects large amplitude fluctuations involving long segments to give rise to truncated rearrangements; step by step, conformational rearrangements of shorter and shorter segments are then progressively effected until all skeletal bonds get eventually locked. Consequently, the broad spectrum of internal chain relaxation times plays a crucial role in determining the rate of freezing in of the free volume as a function of the cooling rate. In agreement with the fact that the glass transition is not a second-order thermodynamic transition, the lowest minima of the potential energies of rotations of skeletal bonds are not fully occupied below T_g in the frozen-in material.

As determined from the measurements described below, the glass transition of polymers generally takes place over a temperature interval of about 20 °C. As usual, T_g increases with increasing cooling rate. In practice, this shift remains smaller than about 10 °C. Besides, this temperature is higher for polymer networks made up of cross-linked chains than for free chains because segments bounded by cross-links explore a restricted array of conformations and also because the presence of cross-links reduces the local free volume.

In partially crystallized polymers, the glass transition of course involves only those parts of chains left out of crystallites. Although it increases with the degree of crystallinity reflecting a reduction of free volume, it always takes place below the melting temperature of the crystal.

5.2 Secondary Glass Transitions

By cooling a polymer below the α glass transition temperature, one can observe one or two secondary transitions, the first designated by β and the second by γ . They reflect the locking of rotational oscillations of skeletal bond occurring in wells associated with minima of the potential energy of rotations, without any jump occurring above energy barriers. The β transition may also reflect local rearrangements of neighboring side chemical groups attached to chain skeletons. The β glass transition temperature is denoted by T_{s1} . Although the following rule is not general, it is usually close to the difference $T_g - C_{2g}$. Besides, another noteworthy feature of great practical interest resulting from these local rearrangements is that glassy polymers are ductile between T_g and T_{s1} .

5.3 Effects of α to γ Transitions

As for other glass-forming liquids, vitrification in polymeric liquids does not involve any symmetry break, and glass transition temperatures are not strictly defined, but rather depend on the property measured. Variations of second-order thermodynamic properties are frequently investigated as they probe the progressive

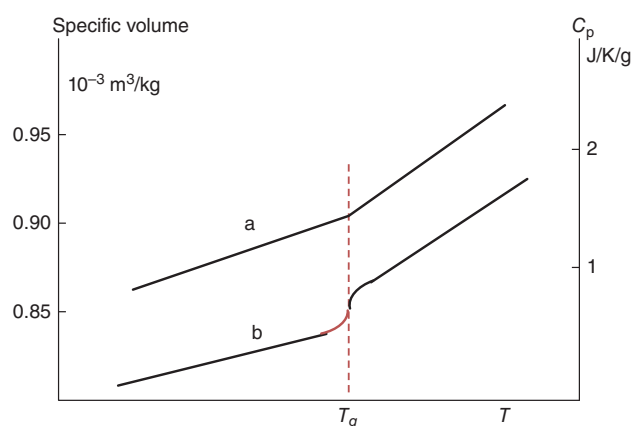


Figure 4 Glass transition as detected in measurements of the specific volume (a) and isobaric heat capacity (b), for which typical values are indicated on a weight basis.

slowing down of the amplitude of the skeletal random motion of polymers.

Upon cooling, this process is clearly reflected by the marked decrease of the thermal expansion coefficient α_v (Figure 4) from about 10^{-3} K^{-1} above T_g to one third of this value below T_g . Likewise, a relatively stronger decrease of the isobaric heat capacity of the order of 0.25 J/K/g takes place in a range of about 10 K, without exhibiting any of the features of a second-order phase transition (Figure 4).

Elastic properties show analogous, albeit more complex variations because of a greater sensitivity to chain rearrangements. Polymeric glasses are brittle and their Young moduli may be as high as 10^9 Pa . Upon heating, the Young moduli of different kinds of polymers show slight but clear decreases at the β and γ secondary transitions and then a sharper decrease at the glass transition (Figure 5). For cross-linked chains forming a permanent network, a plateau at about 10^6 Pa is reached at high temperatures, pointing to reversible deformations 1000 times higher in the rubber than in the glass. For long chains, the Young modulus also exhibits first a reversible plateau at about 10^5 Pa , before flow takes place at higher temperatures. A similar evolution is seen for short chains, but the onset of flow is closer to the glass transition.

The glass transition also affects the local friction coefficient introduced in Section 8.7.3.2. By lowering step by step the reference temperature T_0 in Eq. (8), one can choose the glass transition temperature T_g as a reference to determine subsequently the numerical values of the coefficients C_1^g and C_2^g , analogous to the original coefficients C_1^0 and C_2^0 . For a silicone oil, T_g , C_{1g} , and C_{2g} are, for instance, 150, 6.12, and 69 K ($T_\infty = 81 \text{ K}$), respectively, but the same properties for poly(methyl methacrylate) chains are 276, 18.09, and 54 K ($T_\infty = 222 \text{ K}$),

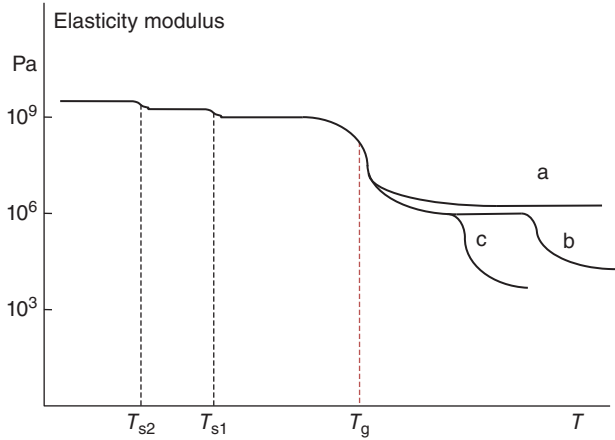


Figure 5 Schematic variations of typical numerical values of elastic moduli shown as a function of temperature. Curve a, polymer network (gel). Curve b, long-chain polymer (number of skeletal bonds higher than 200). Curve c, short-chain polymer. The temperatures of secondary transitions, T_{s1} and T_{s2} , respectively, are shown in addition to the α glass transition temperature T_g .

respectively. As to the fractional free volume f_g/B , it is of the order of 0.025 at T_g for most polymers, whereas the friction coefficient $\zeta_0(T)$ jumps from about 10^{-7} kg/s, at 100 K above the glass transition, to 10^2 kg/s at T_g [7].

Finally, the fact that relaxation timescales become clearly longer than the timescale of experimental measurements when the viscosity becomes higher than 10^{10} – 10^{12} Pa·s has strong effects on the tangent of the loss angle δ (Figure 6), which exhibits a sharp maximum in the glass transition range. Likewise, the smaller peak observed at lower temperatures is associated with a secondary transition.

5.4 Lowering of the Glass Transition

Many solvents of low molecular weight are characterized by a fractional free volume and exhibit glass transitions, like polymers. The addition of good solvents to polymers increases the total free volume of corresponding solutions, whereas the local friction coefficient assigned to monomeric units in each chain diminishes; this effect induces more mobility of macromolecules. At a given temperature, the variation of the fractional free volume f_M with the concentration of the solution is conveniently described by the following equation:

$$f_M(T, T_0, \phi) = \phi f_p(T, T_0) + (1 - \phi) f_s(T, T_0), \quad (9)$$

where f_p and f_s are the fractional free volumes of the polymer and solvent, respectively, and ϕ is the volume fraction of polymer in the solution. By combining Eqs. (2) and (9), one can then obtain the glass transition temperature

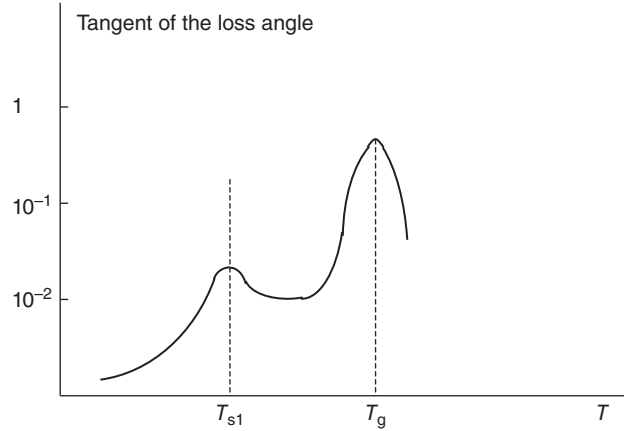


Figure 6 Schematic variations of the tangent of the loss angle across the temperature ranges of the α and secondary transitions.

of the solution, $T_{g,M}$, at which the free volume, $f_M(T, T_0, \phi)$, would vanish:

$$T_{g,M} = \frac{(\phi \alpha_p T_{g,p} + (1 - \phi) \alpha_s T_{g,s})}{(\phi \alpha_p + (1 - \phi) \alpha_s)}. \quad (10)$$

In this equation $T_{g,p}$ and $T_{g,s}$ are the glass transition temperatures of the polymer and solvent, respectively, and α_p and α_s similarly the coefficients of thermal expansion of the free volumes in the polymer and solvent.

5.5 Aging

Depending on the heights of potential energy barriers, the probabilities of rotation of skeletal bonds are not necessarily all zero in the glassy state so that local rearrangements can occur over timescales as long as several years. Viscoelastic responses are particularly sensitive to such an aging when a liquid polymer is cooled down to a temperature intermediate between those of the α and β transitions at which it is then kept for a long time Δ . These responses depend on both the temperature and duration Δ of the aging process [14]. The longer the time interval Δ , the larger the number of bonds subjected to local rearrangements that are progressively locked, giving rise to a decrease of the local fluidity. For example, creep affecting a polymer maintained at a fixed temperature takes place over a timescale τ_F that is an increasing function of Δ .

More precisely, the dependence of the creep effect on the correlation of τ_F with Δ closely follows a law of corresponding states according to which performing any creep measurement at a time t , after a time interval of aging Δ , is tantamount to performing creep measurements at a time t' , after a time interval of aging Δ' , such

that $t'/t = \tau_F(\Delta')/\tau_F(\Delta)$. The ratio $\tau_F(\Delta')/\tau_F(\Delta)$ defines a factor of equivalence “creep timescale/time interval of aging,” which is a power law function of Δ' . It is especially striking that this law is observed at any temperature of aging above the β transition; it is characteristic of viscoelastic responses of polymers.

Finally, it must be kept in mind that, in the absence of additives, most polymers can undergo degradation, which develop during long time intervals of aging and give rise to scissions of skeletal bonds. Degradation depends on the polymer chemical structure and can be induced by many factors. Scission of skeletal bonds can, for example, take place under extreme mechanical stress. Besides, phenyl groups attached to chain skeletons are very sensitive to light because of UV-induced formation of radicals, which in turn react with monomer units. Polymers may in addition be sensitive to oxygen, water, heat, and the presence of impurities, which cannot be completely removed during synthesis. A large variety of chemical mechanisms can cause degradation; in most cases, however, their description is beyond the scope of this chapter as they are still not well understood. The expected effects of additives are to prevent oxidation and/or secondary chemical reactions from occurring [15].

6 Polymer Products

6.1 Transparent Materials

High transparency is sought after in many applications. For this purpose, partial crystallization has to be avoided except when macromolecules are made up of units concatenated with a strong irregularity that prevent chain segments from being ordered. Polymethyl methacrylates ($T_g = 380$ K), polycarbonates ($T_g = 413$ K), and polystyrenes ($T_g = 370$ K) are typical polymers usually synthesized for their high transparency; for example, about 90 % of light is transmitted through the 2 mm thick polycarbonate used to make up optical devices for cars. The transparency of polymethyl methacrylates, used to make rigid contact lenses, is higher than that of ordinary glasses with a 92 % light transmission for a 3 mm thickness. Polymethyl methacrylates have good resistance to dilute solutions of acids or of bases and can be exposed to the elements without undergoing chemical damage; their chemical structure is not modified by exposure to UV light.

6.2 Fibers and Films

Many synthetic fibers, like nylon or Kevlar, poly(paraphenylene terephthalamide), in contrast exhibit a high degree of crystallinity; they consist of uniaxially

oriented, hydrogen-bonded crystalline chains; hydrogen bonds ensure mutual sticking of segments. If the tensile strength of Kevlar fibers (3600 MPa) is much lower than those of carbon fibers (7000 MPa), it is comparable with those of pristine silicate fibers, namely, 2.4–5.0 GPa (Chapter 1.6) and, thanks to their lower density, even higher if considered on a weight basis.

Packaging films are obtained from polymers subjected to a biaxial stretching. Consider, for example, the polymer $[-O-CH_2-CH_2-O-CO-C_6H_4-CO-]_m$, which is made up of units containing the distinct ethylene glycol and terephthalate chemical groups whose melting and glass transition temperatures are 538 and 343 K, respectively. The polymer is first lengthwise stretched between these two temperatures at 363 K; then, it is subjected to a lateral stretching at 393 K to give rise to a transparent film with a resulting thickness of 50 μm . The crystallinity then is about 50 %, the residual glassy phase sticking the chains together. In this case there is no light diffusion because the size of crystallites is lower than the wavelengths of visible light.

6.3 Polymeric Foams

One obtains the cellular structure of foams by adding a swelling agent during polymer synthesis; this agent may be water vapor or a chemical product releasing nitrogen or carbon dioxide upon heating. The specific mass of a foam varies from 10 to 100 kg/m^3 to be compared with the typical 10³ kg/m^3 of a bulk polymer. The foam is rigid as long as it is kept at temperatures much lower than T_g . Of interest is the fact that rigid foams exhibit damping of mechanical oscillations and a response to a uniaxial squeeze characterized by both a large compression ratio and a small lateral dilation. Polyurethane foam, a typical example, is synthesized from the reaction of two-functional isocyanate molecules $[O=C=N-R-N=C=O]$ with an alcohol $[OH-R'-OH]$, giving rise to a release of carbon dioxide that originates from the pores; three-dimensional structures are obtained when a three-functional alcohol is used.

6.4 Porous Membranes and Hollow Fibers

Porous membranes represent one of the most remarkable polymer products. Their porosity is achieved with the so-called phase inversion process. In a first step the polymer, poly(ether imide), for example, is diluted in a solvent in *N*-methyl pyrrolidinone such that the glass transition range of the resulting solution is much lower than room temperature. The solution is then quickly immersed in a bath – usually water – which has a strong affinity for the solvent but no affinity at all for the polymer. As a result, the solvent is progressively extracted from the solution,

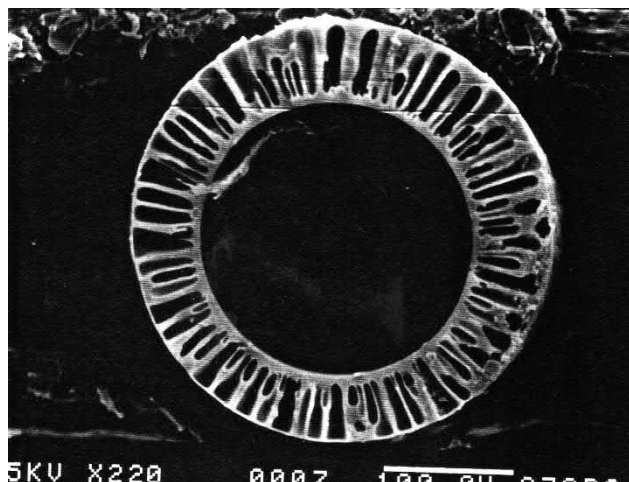


Figure 7 Porous, hollow Dralon® fiber prepared from polyacrylonitrile $[(C_3H_3N)_n]$.

but the long macromolecular chains prevent them from diffusing rapidly enough to yield a homogeneous polymer phase [12]. The separation takes place instead between a polymer-poor microphase and a water- and solvent-rich microphase on the one hand and between a polymer-rich microphase and a water- and solvent-poor microphase on the other hand. With the appropriate concentration of solvent, the solvent-rich phase gathers as droplets enclosed by walls made up of the concentrated polymeric microphase. Through the extraction of solvent, the polymer concentration increases in the walls whose glass transition temperature rises above room temperature according to Eq. (10). The polymer medium then gets frozen; the remaining solid is made of connected pores with glassy walls. As applied to hollow fibers (Figure 7), the phase inversion process is used to make artificial kidneys consisting of about 8000 fibers put all together in dialysis machines where they are fully compatible with blood. For medical applications, membranes can even be formed with a porosity fitted to the size of bacteria.

6.5 Mineral Particles and Polymer Mixtures

The mechanical properties of polymers can be improved with mineral particles on which the macromolecular chains, connected to one another by chain segments, are partly adsorbed to form a three-dimensional network. The adsorption process of any chain on a particle embedded in a molten polymer results from the formation of an average number of contacts onto the surface equal to the square root of the number of monomer units per chain [12]. Adsorbed chains cannot be easily displaced upon stretching of the mixture, for example; the

stronger the chain-particle adhesion, the stronger, of course, the effect.

Addition to a liquid polymer of mineral particles such as silica or carbon, characterized by a specific area of the order of $150 \text{ m}^2/\text{g}$ resulting from fractal surfaces, enhances the Young modulus in the glassy state by a factor of up to 10. As another example, addition of 40 wt % silica particles to silicone yields a Young modulus of the order of 10^{10} Pa ; conversely, however, stretching at failure may then be reduced by a factor of 10 from 0.3 to 0.03. As to the cohesion of films, one usually enhances it by adding mineral particles whose concentrations remain low enough to ensure transparency.

7 Perspectives

As a convenient way to summarize the tremendous advances made in polymer science, the reader can be reminded that the existence of macromolecules as physical subsystems was recognized only about 80 years ago. New macromolecules keep being created with in particular the aim of improving heat resistance and mechanical properties. As illustrated by the preceding discussion, a deep understanding of polymers is a prerequisite to control the glass transition and, in turn, the properties of the glass state on which particular applications rely.

Particular attention is currently being paid to packaging plastics, aiming, for instance, at reducing food waste, while syntheses of new thin films acting as semipermeable barriers specific to solids, liquids, or gas are in continuous progress. Considering membranes, the stress is laid on a better control of pore size distributions fitted to separation processes such as microfiltration for biomedical research, hyperfiltration for desalination, or ultrafiltration. Besides, perfluorinated ionomer membranes are used as electrolytes for electrochemical processes occurring, for instance, in batteries. Finally, it is worth emphasizing that water-based polymers in the form of colloidal particles dispersed in an aqueous medium, called latexes, will keep their wide variety of applications in paints, adhesives, foams, and coatings.

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8.8

Introduction to Polymer Chemistry

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1 Introduction

With a world production that has almost tripled since 1990 to reach about 335 million tons in 2016, man-made polymers are ubiquitous. They may be clearly visible as in packaging, casings for electronic equipment, toys, and cars or, in contrast, “hidden” in paints, polymer-modified concrete and asphalt, glue joints, or textile blends. The reason for this diversity of uses is that these materials range from liquids to waxes and infusible solids as well as from elastomers to brittle solids. Such a diversity of properties (Table 1) is unique to these materials, even more so since the desired properties can be precisely tailored by a combination of chemistry and processing.

Improperly, these important materials are often called *plastics* or, in German, *artificial material* [Kunststoff]. Epoxies and phenolics do show that they are not necessarily *plastic* in a physical sense, whereas cellulose, spider silk, and DNA indicate that they do not have to be artificial. Hence, they are better termed *polymers* because they are composed of many [πολύς] parts [μέρη]. These are monomers [μόνο, single, and again μέρος, part], which add up as *repeats* to form large, chain-like macromolecules (Chapter 8.7, [6, 7]). The macroscopic properties of polymers originate in the molecular properties of the chains such as the average degree of polymerization ($\bar{X}_n$), composition, geometric factors along the chain, and polarity, which determine the molecular arrangement and cohesion in the solid state. In view of the broad range of properties and structures, it is virtually impossible to provide a set of general design rules for polymers.

Generally, increasing the number of repeat units increases the mechanical properties and the viscosity. The chemical properties of the monomers translate mostly into those of the corresponding polymers, although some water-soluble monomers such as acrylonitrile or *N*-acetylglucosamine can form partially (PAN) or totally water-insoluble polymers (chitosan). The solid-state properties are mostly associated with the glass transition temperature and all effects that act on it also affect the mechanical properties. Beyond that, every field of application operates on their own set of findings and models. To complicate this even further, technical polymers are often blends of two or more homo- or copolymers rather than one homopolymer made from a highly sophisticated monomer. In blends, however, the optimum composition is often determined experimentally.

Polymers can be classified in a number of ways. Here a molecular approach will be adopted through consideration of the mechanism of backbone formation, i.e. the sequence in which monomers assemble into higher-molecular-weight compounds. In a more technical sense, polymers are frequently classified by their macroscopic properties according to the degree of cross-linking. In this respect, polymers are either non-cross-linked *thermoplastics* or cross-linked *thermosets* and *elastomers*. A major feature is that polymer chains are not uniform, but follow a length distribution such as that of Schulz–Flory (Figure 1) commonly observed in industrial processes. The maximum of the distribution represents the average degree of polymerization and yields the molecular weight after multiplication by the mass of the repeat unit. But different properties do not vary in the same way with the degree of polymerization, so it is necessary to distinguish, for instance, weight (w) and viscosity (η) averages, which are found at higher degrees of polymerization.

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Table 1 Density, glass transition and melting temperatures, ultimate tensile strength and Young’s modulus of commodity, engineering, and high-performance polymers.^a

	ρ (g/cm ³)	T_g (°C)	T_m (°C)	β (MPa)	E (GPa)
Commodity					
PE LD	0.915–0.93	–78 ^{b,c}	101	7–17	0.14–0.3
PE HD	0.94–0.97		125	20–40	0.7–1.4
PP	0.85–0.95 ^d	–12 to –4 ^e	138–160 ^e	30–40	1.1–2.0
PMMA	1.17–1.20	106	— ^f	55–75	2.5–3.3
PS	1.04–1.08 ^e	95	240 ^e	30–60	2.4–3.2
PVC	1.32–1.52	98	— ^f	40–75	1.0–3.5
Engineering					
PA6	1.13	43–52 ^b	220	80 ^g	3 ^g
PA6,6	1.14	50 ^b	255	75–90 ^g	3.4 ^g
PAN	1.14–1.19	65–145 ^d	319	250–940 ^f	2.8–19
PC	1.2	146	270	70–90	2.1–2.4
PEEK	1.32	150	340	90–200	3.6
PET	1.29–1.40	70	265	50	3.0

^a Data from [1, 2] except otherwise noted.
^b Conflicting data, most common vales given.
^c Value from [3] corroborated by molecular dynamic methods in 2016.
^d See also Table 3.
^e T_g of PAN strongly influenced by the type of preparation (cf. [5]); typical value for intermediate molecular weights prepared in water is approx. 87 °C.
^f Value for fiber-grade material.
^g Properties for dry-molded specimen.

Another important parameter is the width of the distribution (D), which is characterized by the ratio of weight to number (n) average:

$$D = \frac{\overline{X}_w}{\overline{X}_n} = \frac{\overline{M}_w}{\overline{M}_n}. \tag{1}$$

This is called the dispersity (previously polydispersity or polydispersity index). The Schulz–Flory distribution (Figure 1) is characterized by $D = 2$. As an example, a material produced by free-radical polymerization with an average $\overline{X}_n$ of 2000 contains about 5 and 0.2 ppm of chains with a $\overline{X}_n$ of 20 and 20 000, respectively. In contrast, natural proteins have $D = 1.000$ [unity]. Even modern synthetic methods cannot accomplish such a level of control, however, let alone the precision in controlling the architecture.

Acronyms

ABS acrylonitrile butadiene styrene. Either blend of SAN and NBR or graft copolymerization of acrylonitrile ($\text{CH}_2=\text{CHCN}$) and styrene ($\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$) onto NBR particles.

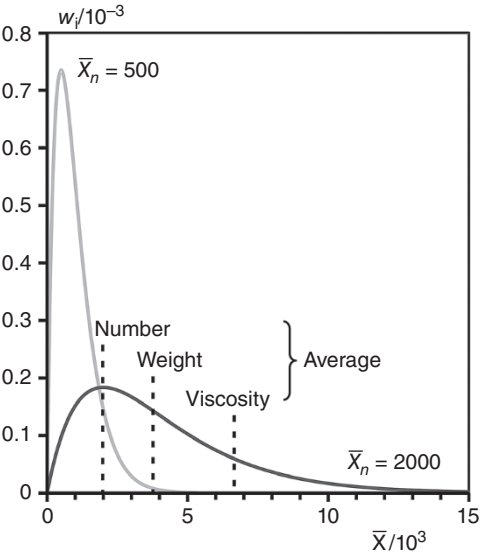


Figure 1 Schulz–Flory distribution for polymers with a degree of polymerization $\overline{P}_n = 500$ (light curve) and $\overline{P}_n = 2000$ (dark curve). Positions of the number, weight, and viscosity averages along the distribution indicated for the higher-molecular-weight polymer.

CA	cellulose acetate. Thermoplastic polymers obtained by acetylation of cellulose.	PiB	poly(isobutylene).
CR	chloroprene rubber. Chemically poly(2-chlorobuta-1,3-diene, $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$), better known as neoprene.	PMMA	poly(methyl methacrylate).
EP	epoxy. Formed by cross-linking epoxy resins, mostly bisphenol A epichlorohydrin pre-polymer, with polyamines.	POM	poly(oxymethylene), $\{\text{CH}_2\text{O}\}_n$.
EPR	(or EPM) ethylene propylene rubber. Random copolymer of ethylene ($\text{CH}_2=\text{CH}_2$) and propylene ($\text{CH}_2=\text{CHCH}_3$).	PP	poly(propylene).
EVA	poly(ethylene-co-vinyl acetate). Vinyl acetate ($\text{CH}_2=\text{CHOCOCH}_3$) content from 0 (pure PE) to 100% (pure PVAc). Low contents blended with PE to increase failure strain; used as hot melt at intermediate contents; rubbery, similar to plasticized PVC beyond 30% vinyl acetate.	PS	poly(styrene).
NBR	nitrile butadiene rubber. Copolymer of acrylonitrile and butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$).	PTFE	poly(tetrafluoroethylene), $\{\text{F}_2\text{C}-\text{CF}_2\}_n$.
PA $x(y)$	polyamide. Containing amide bonds $-\text{CO}-\text{NH}-$; x and y , numbers of carbon atoms of the monomer(s), e.g. PA6,6 [poly(hexamethylene adipamide)], PA6 [poly(ϵ -caprolactam)].	PU	polyurethane. Containing the urethane unit $-\text{O}-\text{CO}-\text{NH}-$.
PAN	poly(acrylonitrile).	PVA	poly(vinyl alcohol), $\{\text{CH}_2-\text{CHOH}\}_n$.
PB	poly(butadiene).	PVAc	poly(vinyl acetate), $\{\text{CH}_2-\text{CHOCOCH}_3\}_n$.
PC	polycarbonate. Containing carbonate unit $-\text{O}-\text{CO}-\text{O}-$, but usually referring to poly(oxy-carbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene), the condensation product of phosgene and bisphenol A.	PVB	poly(vinyl butyral).
PDMS	poly(dimethylsiloxane). Made from either dichlorodimethylsilane ($\text{Cl}_2\text{Si}(\text{CH}_3)_2$) by polycondensation or cyclic dimethylsiloxanes ($\{\text{Si}(\text{CH}_3)_2\text{O}\}_n$ with $n = 5, 6$) by ring-opening polymerization.	PVC	poly(vinyl chloride), $\{\text{CH}_2-\text{CHCl}\}_n$; abbreviated as PVC-P [P = plasticized] and PVC-U [U = unplasticized] or as S-PVC [S = suspension polymerization] and M-PVC [M = bulk polymerization].
PE-HD	high-density poly(ethylene).	SAN	copolymer of styrene and acrylonitrile, similar to PS in properties, but with $T_g > 100^\circ\text{C}$.
PE-LD	low-density poly(ethylene).	SBR	styrene butadiene rubber.
PEO	poly(ethylene oxide), $\text{HO}[\text{CH}_2-\text{CH}_2-\text{O}]_n\text{H}$; low-molecular-weight types sometimes called poly(ethylene glycol) (PEG) because of chemical kinship with ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$.		
PES	polyethersulfone, a class of high-performance polymers of the general type $\{\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2\}_n$.		
PET	poly(ethylene terephthalate), $\{\text{OC}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{O}\}_n$. Most prominent member of the polyester family mainly used for beverage bottles and in textile industry where it is abbreviated PES despite the potential mix-up with polyethersulfone.		

2 Polymer Synthesis

The formation of polymers from small molecules can proceed by two principal mechanisms, namely, step and chain growth (Figure 2). Which of these two mechanisms the synthesis follows is solely determined by the type of monomers; only very few polymers can be synthesized by both mechanisms, albeit from different monomers. Polymers formed by chain-growth reactions can be thermoplastics (e.g. PMMA) or thermosets (e.g. resin-based dental cements). Likewise typical step-growth polymers can be either thermoplastics (e.g. PA6,6) or thermosets (e.g. epoxy).

2.1 Chain-Growth Polymerization

Chain growth is characterized by a single *active* site normally at the end of the chain, to which monomers add, just like pearls are threaded on a string. The formation of the polymer only occurs at these sites and only while the site is active. Once the active site is lost, polymerization can continue only if a new one forms. As a consequence, chain growth can be divided into the three main stages of *initiation* [generation of an active site], *propagation* [chain growth], and *termination* [loss of active site]. This mechanism most commonly applies to unsaturated monomers such as propylene or styrene and will be explained using the example of *free-radical* polymerization.

Initiation begins with the decomposition of suitable molecules called initiators, abbreviated as Ini_2 . Common

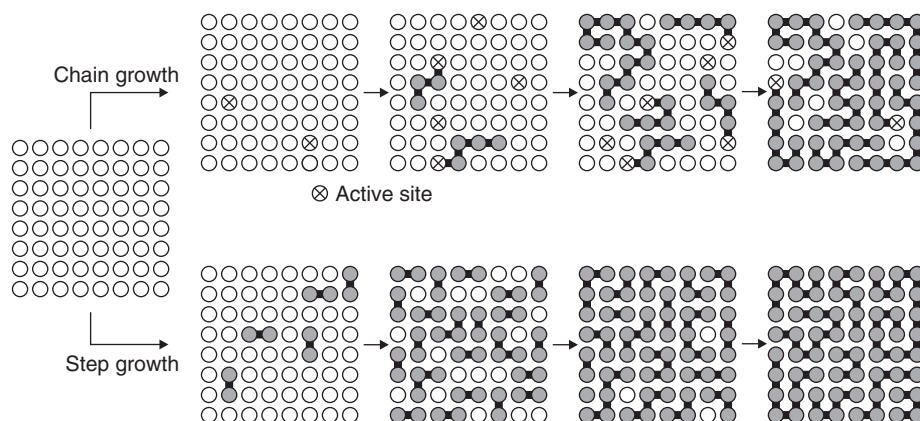
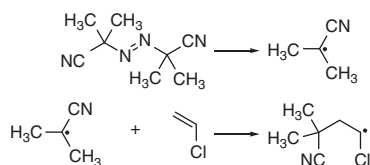
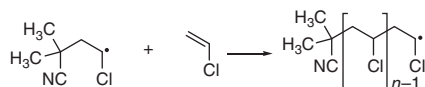


Figure 2 Schematic representation of the chain-growth (top) and step-growth (bottom) mechanisms. ⊗ indicates the active site in the chain-growth mechanism.

Initiation



Propagation



Termination

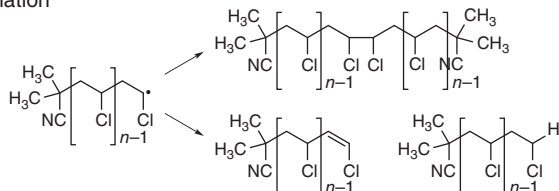


Figure 3 The three main phases of free-radical polymerization illustrated by PVC with AIBN initiator.

ones are 2,2'-azobis(*iso*-butyronitrile), AIBN, dibenzoyl peroxide, DBPO, and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, KPS). The decomposition of initiators leads to the formation of radicals, which then add to the monomer (Figure 3) to create the active site of the chain, which is the terminal atom bearing an unpaired electron: this is why the process is termed *free-radical* polymerization. Through propagation, monomers add to the active site, thereby increasing the number of repeat units in the chain and building up molecular weight. The regular mode of termination is either *combination*, in which two active sites combine to form a chain of double molecular weight, or *disproportionation*, which is the transfer of a hydrogen atom from one chain to the active site of a second chain. This exchange leaves one polymer with an unsaturated

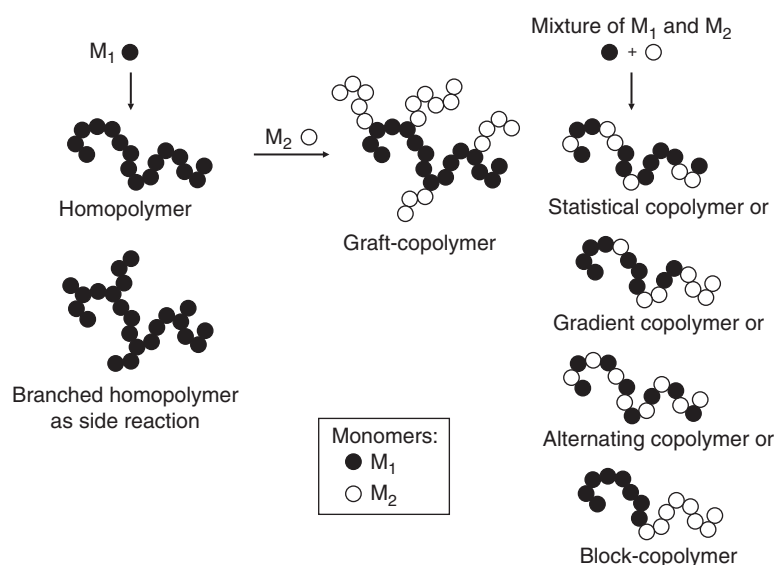
end and the other with a saturated end, so it does not modify the molecular weight of the chains. In this context, termination always refers to individual chains and not to the reaction as a whole. Macroscopically observable polymerization thus proceeds as long as the initiation process supplies new radicals.

At low conversion rates, a steady state is obtained upon propagation such that the rates of initiation and termination are equal, i.e. the number of active sites is constant. The resulting molecular weight then is inversely proportional to both the rate of polymerization and the initiator concentration. As a result, increasing temperature or adding more initiators results in shorter chains.

Radicals are highly reactive species so they can undergo a number of side reactions. Depending on experimental conditions (e.g. temperature, solvent quality), the initiator radicals may recombine without starting a chain, in which case radical sites are annihilated as termination reactions also do. On the other hand, *transfer* reactions such as removal of a H atom by reaction of a radical with a C–H bond (i.e. H-abstraction) do preserve the unpaired electron. Provided the new species is of sufficient reactivity, it can serve as an active site to keep polymerization going. Transfer can involve any compound present in the reaction mixture, including solvent, monomer, and polymer. The latter, however, causes branching. When uncontrolled, transfer reactions usually have negative effects on polymerization such as lower molecular weight and conversion or increased branching. On the other hand, transfer reactions are sometimes deliberately induced by the addition of transfer agents in order to control the molecular weight or afford polymers with functional chain ends. Examples are fluorotelomer alcohols (FTOH), for instance, used in fire-protecting foams and stain-resistant coatings or in the production of synthetic rubber to which thiols are added to control molecular weight.

Chain-growth polymerization, and especially free-radical polymerization, is not limited to single monomers. In fact,

Figure 4 The greater variety of molecular architectures obtained by binary copolymerization with respect to homopolymerization.



a large number of industrial materials are copolymers made from monomer mixtures. Because the molecular weight and degree of branching of homopolymers are difficult to control, copolymers have the major advantage of offering an enormous variety of possibilities to tune macroscopic properties through control of not only the

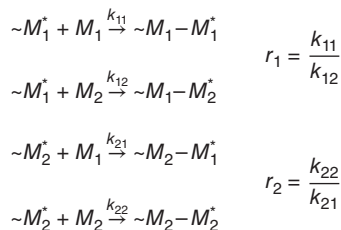


Figure 5 Terminal model of binary copolymerization. The four possible combinations are characterized by rate constants, which are then combined to reactivity ratios r indicating the tendency of an active site for homopolymerization vs copolymerization. Polymer chain symbolized by “~.”

polymer composition but also of the molecular architecture (Figure 4).

Copolymerization of monomer mixtures under chain-growth conditions proceeds like homopolymerization. In a mixture of two monomers, M_1 and M_2 , however, the active site formed in the previous step from M_1 or M_2 can now add to the same kind of monomer or to the other. This approach, which only considers the rate-determining chain ends, is called the terminal model and operates on four kinetic constants (Figure 5). These are combined to two reactivity ratios $r_{1,2}$, which express the tendency of a chain end to form homo- or heterodiads, diad in this context referring to two consecutive repeat units. The values of r_1 and r_2 relative to each other determine the architecture of the resulting polymer (Table 2).

As a result of improved properties, a large number of modern polymer materials are copolymers. The SAN copolymer of styrene and acrylonitrile, for instance, exhibits a higher strength and a better scratch and crazing

Table 2 Values of the reactivity ratios $r_{1,2}$ and resulting polymer architecture.

Ratios	Description	Example
$r_1 = r_2 = 1$	Ideal statistical copolymerization	Acrylamide/acrylonitrile $r_1 = 1.08, r_2 = 0.97$
$r_1 = r_2 = 0$	Strict alternating copolymerization	Maleic anhydride/vinyl acetate $r_1 = 0, r_2 = 0.019$
$r_1, r_2 < 1$	Statistical copolymerization, but polymer composition changes with reaction time	Styrene/acrylonitrile (SAN) $r_1 = 0.29, r_2 = 0.02$
$r_1 < 1, r_2 > 1$	M_2 blocks interrupted by short M_1 blocks	Styrene/1,4-butadiene (SBR) $r_1 = 0.83, r_2 = 1.83$
$r_1, r_2 > 1$	Long alternating blocks of M_1 and M_2	Not observed in radical polymerization

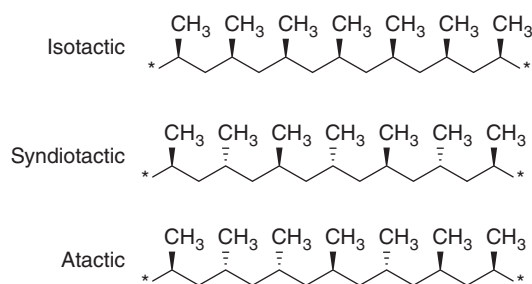


Figure 6 The three principal stereoisomers made from vinyl monomers with a single substituent (using PP as an example). Wedged and dashed bonds pointing to substituents in front of and behind the plane, respectively.

resistance than PS. Like PS, however, SAN is brittle, but it can be modified with a butadiene acrylonitrile copolymer to form ABS, a *terpolymer alloy*, which shows an improved impact resistance. Likewise, numerous modern synthetic rubbers are copolymers such as ethylene vinyl acetate (EVA), ethylene propylene (EPR), styrene butadiene (SBR), and acrylonitrile butadiene (nitrile rubber, NBR).

With very few exceptions (e.g. ethylene), the most common monomers used in radical polymerization carry a single substituent at the double bond. Upon polymerization the geometry at the terminal carbon changes from trigonal (the active site) to tetragonal (the polymer chain) so that two consecutive substituents can end up on the same or different sides of the chain. The phenomenon is called *tacticity*. It gives rise to three principal stereoisomers (Figure 6) depending on whether all substituents are on the same side [*isotactic*], on strictly alternating sides [*syndiotactic*], and are randomly distributed between the sides [*atactic*]. In free-radical polymerization, the stereochemistry cannot be controlled, so such polymers are highly atactic. Tacticity is controlled through coordination polymerization with transition metal catalysts, often based on titanium or zirconium (the Ziegler–Natta catalysts), whose metal center determines a predefined coordination orientation for the monomer and chain.

Such a molecular engineering has been an outstanding achievement to control material properties through

Table 3 Macroscopic properties of the stereoisomers of poly(propylene) and poly(styrene).

Polymer	Stereoisomer	T_g (°C)	T_m (°C)	ρ (g/cm ³)
Poly (propylene) ^a	Isotactic, crystalline	−12	163	0.92
	Syndiotactic, crystalline	−4	130	0.95
	Atactic, amorphous	−7	—	0.85
Poly(styrene)	Isotactic, crystalline	—	240	1.08
	Atactic, amorphous	95	—	1.04

^a Thermal data for polypropylene [4].

stereochemistry. For example, atactic PP and PS are amorphous thermoplastics with moderate softening temperatures, whereas their isotactic isomers are semicrystalline thermoplastics with considerably higher melting points (Table 3).

The chain-growth mechanism is, however, not limited to free-radical polymerization of unsaturated monomers. It is also followed by anionic and cationic polymerization of olefins; a commercial example of the latter is the production of butyl rubber, which is prepared by cationic polymerization of isoprene-containing mixtures between −40 and −100 °C in hexane. In addition, ring-opening polymerizations of cyclic monomers such as ϵ -caprolactam to PA6 and ethylene oxide to poly(ethylene oxide) proceed via successive addition of monomers to an active site – hence a chain-growth mechanism – although the resulting polymers have the appearance of step-growth products (Figure 7).

2.2 Step-Growth Polymerization

One fundamental difference between step and chain growth is that the former does not involve active sites in the way chain-growth polymerization does. In a mixture of molecules bearing more than one functional group, reaction can occur between any two suitable molecules to produce first dimers and then trimers, tetramers, and so on. If the functional groups are denoted by A and

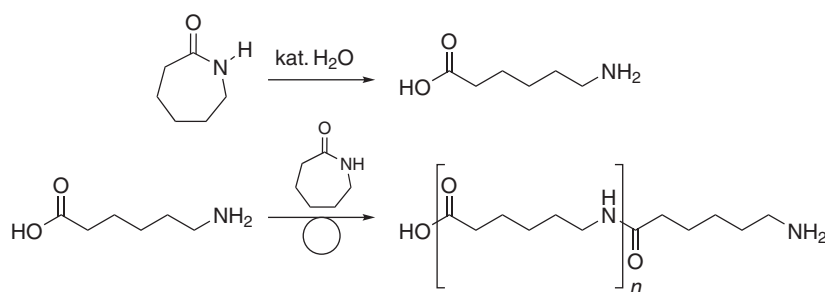


Figure 7 Chain-growth mechanism exemplified by the ring-opening polymerization of PA6 from ϵ -caprolactam.

B, the assumption is that both A and B react only unlike units. Thus, monomers of the sort AB, such as lactic acid or amino acids, form polymers of the type $-AB-AB-AB-$, where “-” denotes the newly formed bond. In contrast, mixtures of AA (e.g. diols) and BB (e.g. diacids or diisocyanates) form polymers of the type $-AA-BB-AA-$. These two polyamides may seem similar, but the small differences between their molecular structures do cause the noticeable differences in macroscopic properties apparent in Table 1 between PA6 (made from the AB precursor ϵ -caprolactam) and PA6,6 (made from 1,6-diaminohexane and adipic acid).

A second fundamental difference between chain and step growth is that there is no termination in the latter. The chains can theoretically keep growing until no unreacted functional groups A and B remain in solution, although this is not observed in practice. Owing to the following kinetic scheme, the correlation between the conversion p and the degree of polymerization $\bar{X}_n$ is rather simple:

$$\bar{X}_n = \frac{1}{1-p} \quad \text{with } p = \frac{N_0 - N_t}{N_0}, \quad (2)$$

where N is the number of unreacted functional groups at the beginning ($t = 0$) and at time t during the reaction. This equation was first proposed by W. Carothers in the 1930s [8]. It clearly indicates that high-molecular-weight polymers are obtained only at high conversion in step-growth polymerization (Figure 8). For example, PA6,6 fibers require $\bar{X}_n > 110$ for sufficient mechanical strength, which corresponds to $p > 99\%$. Conversions of this extent without side reactions are a real challenge

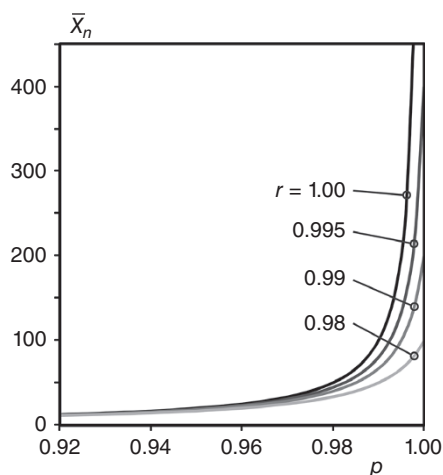


Figure 8 Step-growth polymerization as described by the Carothers equation (black line) for the average degree of polymerization. High values obtained only at high conversions. Significant decreases caused by even slight deviations from the ideal 1:1 stoichiometry (gray lines).

for the toolbox of preparative chemists. It is therefore not surprising that until now, only four known reactions yield high-molecular-weight polymers under step-growth conditions. These are the *Schotten–Baumann* reaction, a polycondensation at the oil–water interface mainly used as a show experiment; the dehydration of salts, used for the preparation of PA x,y polyamides; transesterification used for the preparation of polyesters; and the polyaddition of diols to diisocyanates used for the preparation of polyurethanes.

Actually high-molecular-weight polymers are not always wanted, since they are difficult to process, whereas low-molecular-weight compounds might not exhibit the desired mechanical properties. A mechanism to control the degree of polymerization is therefore desirable. Rapid cooling allows the polymerization to be stopped at any given point, but a more elegant control arises from the fact that Eq. (2) is only valid for mixtures with an exact 1:1 stoichiometry. Intentional or unintentional deviations from the ideal ratio automatically cause a decrease in the degree of polymerization, since all chains will ultimately have the same type of end group. This situation is described by the modified Carothers equation:

$$\bar{X}_n = \frac{1+r}{1+r-2rp}. \quad (3)$$

where r , the molar ratio of monomers, needs to be lower than 1 (Figure 8). One may thus obtain the desired molecular weight by properly adjusting r and allowing the reaction to end naturally.

One achieves the opposite effect, namely, increasing the molecular weight, by adding monomers with more than two functional groups to the reaction mixture. By introducing an average functionality f_{av} ,

$$f_{av} = \frac{\sum n_i f_i}{\sum f_i}, \quad (4)$$

where n_i is the number of moles of the reactant with the functionality f_i , one rewrites the Carothers Eq. (2) as

$$\bar{X}_n = \frac{2}{2 - pf_{av}}. \quad (5)$$

For example, a mixture for preparing an aliphatic polyester containing 1 mol of adipic acid, 0.8 mol of ethylene glycol, and 0.2 mol of glycerol ($f_i = 3$) has $f_{av} = 2.1$ and reaches $\bar{X}_n = 400$ at 95% conversion, whereas a 1:1 mixture of adipic acid and ethylene glycol would still be at $\bar{X}_n = 20$. From Eq. (5) it follows that the degree of polymerization becomes infinite when $pf_{av} = 2$. At this point the polymer becomes a gel, i.e. it forms a quasi-infinite network. The corresponding conversion limit can be written as

$$p_G = \frac{2}{f_{av}}. \quad (6)$$

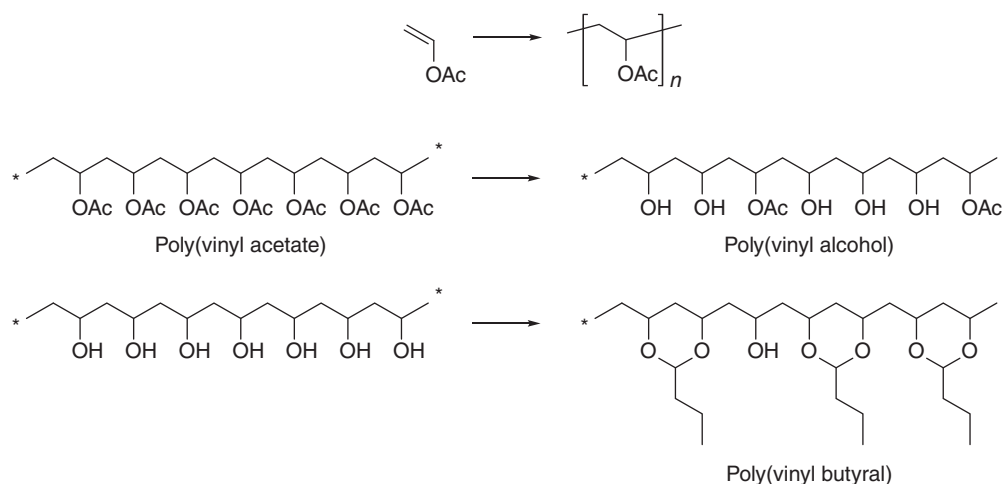


Figure 9 Preparation of poly(vinyl acetate) and subsequent polymer analogous transformations to poly(vinyl alcohol) and poly(vinyl butyral).

Careful experiments have shown that Eq. (6) slightly overestimates the conversion required for gelation because those macromolecules having an X_n value higher than the average value of the mixture gel earlier.

Stepwise growth of the chains is the underlying mechanism in both polycondensation and polyaddition. The difference between them is that small molecules such as water or hydrochloric acid are formed in the former, which need to be removed from the reaction mixture to shift the equilibrium in the right direction. Both polycondensation and polyaddition are important technological processes: a number of commodities such as epoxy, phenolic, melamine, urea-formaldehyde resins, and polyurethanes are prepared by polyaddition, whereas most high-performance polymers such as polyethersulfone (PES) ($T_g = 225^\circ\text{C}$), polyether ether ketone (PEEK) ($T_g = 150^\circ\text{C}$), polyamide (decomposition temperature in air $>550^\circ\text{C}$), and polybenzimidazole (PBI) ($T_g = 425^\circ\text{C}$) are made by polycondensation.

2.3 Polymer Analogous Reactions

When designing polymers for specific applications, the preeminent way is to assemble the chains from suitable low-molecular-weight monomers with one of the two aforementioned mechanisms. There is a third way to tune properties, however, namely, through conversion of one polymer into a second one without deliberate alteration of the degree of polymerization. The most prominent examples of these *polymer analogous* reactions (Figure 9) are the preparation of poly(vinyl alcohol) (PVA) from poly(vinyl acetate) (PVAc), the conversion of PVA to poly(vinyl butyral) (PVB), and the preparation of the cellulose acetate (CA) and cellulose nitrate families.

The reasons for making use of these reactions are manifold. In the case of PVA and PVB, the polymers cannot be prepared by direct polymerization. Vinyl alcohol, the hypothetical monomer of PVA, tautomerizes to acetaldehyde with an equilibrium constant $K \approx 10^{-7}$, whereas PVB cannot be made by direct polymerization of a particular monomer.

Reactions with functional groups at the polymer backbone can be slower or faster than with similar groups in low-molecular-weight compounds. An increased rate is usually the result of neighboring group participation and is, for instance, observed in the alkaline hydrolysis of PVAc, which leads to a pronounced blockiness of the resulting PVA–PVAc copolymer; the acidic hydrolysis does not show this effect and gives rise to a random copolymer instead. More frequently, however, polymer analogous reactions suffer from retardation. In order to react, the reactants have to find and approach each other on a defined trajectory. Polymers usually have low diffusion coefficients in solution and increase the viscosity of the reaction medium, which are both detrimental to the reaction rate. In addition, polymers in solution adopt coiled conformations so that only the outermost functional groups of the backbone are easily accessible. The backbone, which commonly carries substituents at every other carbon atom, also imposes a considerable steric constraint on the reaction trajectory.

3 Polymerization Processes

For polymerization processes, the primary issue is interestingly not chemical, but technical, concerning the continuous or batch nature of the production [9]. The former

is economical only for large-scale commodities or designated specialties, but not suitable for all polymerization mechanisms and/or all monomers. As a matter of fact, PS, SAN, and PMMA molding compounds are frequently produced continuously [10], whereas most other processes are run semi-batchwise.

A second issue is whether processes should be single- or multiphase. The former include bulk, melt, and solution, whereas the latter are realized in the form of emulsions or suspensions. Since most of the monomers used in radical polymerization are liquid, the simplest way to process them is in the bulk, i.e. without any diluting agent. Under these conditions, the volume concentration of the monomer is maximized so that high initial rates of polymerization are achieved. Bulk polymerization can proceed in two distinct ways: if the polymer is insoluble in the monomer, it will precipitate once the limiting molecular weight is reached and polymerization continues in the remaining liquid phase. This is, for instance, observed for the bulk polymerization of vinyl chloride. If the polymer is soluble, the liquid phase becomes increasingly viscous upon polymerization owing to the formation of high-molecular-weight products. As a consequence, the steady-state conditions quickly cease to be respected. The rate of polymerization increases already at fairly low conversions, instead of decreasing as expected for continued initiator and monomer consumption (Figure 10).

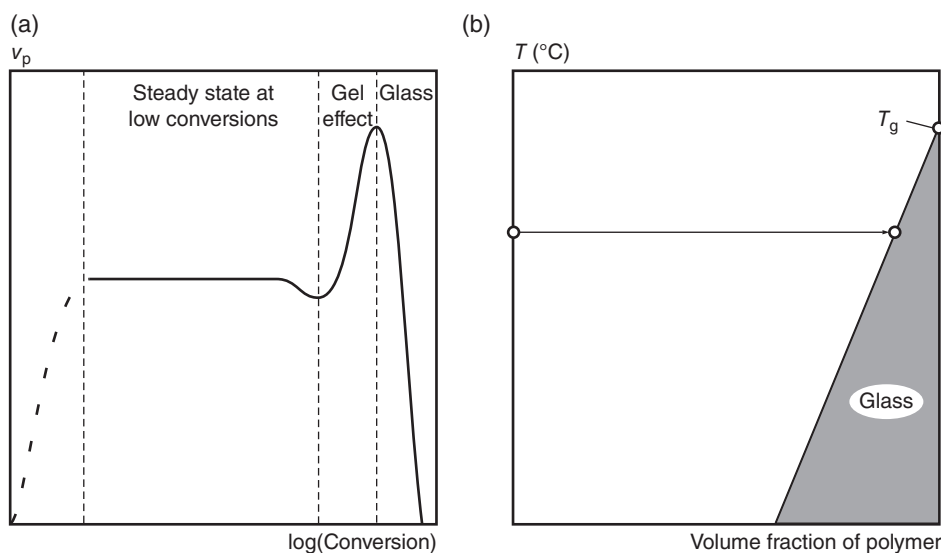
This *gel* or *Trommsdorff–Norrish* effect is caused by the high viscosity of the mixture, which impairs the bimolecular termination of the growing chains [11]. Further polymerization deprives the mixture of more and more monomer, however, which reduces the plasticizing effect of the monomer. If the glass transition temperature of the polymer is higher than the reaction temperature, the mixture becomes glassy and polymerization stops,

leaving unreacted monomer. These drawbacks, along with trace amounts of harmful monomers in the product, the tendency to form high-viscosity gels, and also difficult heat control, are the reasons why radical polymerization in the bulk is rare in industrial production. One of the few exceptions is the production of high-quality acrylic glass sheets in a process called batch-cell bulk polymerization, where bulk polymerization is the method of choice, followed by a posttreatment of the sheets at temperatures above T_g to reduce the residual monomer content.

Step-growth polymerization such as polycondensation is in contrast frequently run in the melt because they are – with few exceptions – slower than radical polymerization. A common process to produce the PET used in the textile industry is melt condensation at about 280 °C in vacuum. As outlined above, high-molecular-weight polymers are only formed at high conversions in step-growth reactions, so the mixture remains at a low viscosity throughout most of the process.

Another important feature of radical polymerization is its highly exothermic nature, except in the cases of incomplete conversions and residual monomers. Bulk polymerization thus suffers from problematic heat dissipation, which could ultimately cause thermal runaway, particularly at larger scales. The simplest way to circumvent the difficulty is to dilute the reaction mixture with an inert solvent that dissolves both monomers and polymer, but a potential side effect then is chain transfer to the solvent, which lowers the degree of polymerization. This procedure is actually the most common in the laboratory, but it is not much adopted in industry because of safety and environmental issues raised by organic solvents. An exception is PVAc, which is frequently prepared in solution; at the end of the reaction, then either the solvent

Figure 10 Rate of polymerization as a function of monomer conversion (a) at a given temperature (e.g. horizontal line in b) and temperature dependence of the point at which the reaction mixture becomes glassy and polymerization stops (b).



is recovered and reused, or the solution is sold as it is (e.g. for solvent-based adhesives).

For environmental reasons, the most desirable medium to run polymerizations is water, which has the added advantage of having an enormous heat capacity. Some monomers such as epoxides and isocyanates are sensitive to water, whereas the most common monomers for radical polymerization are immiscible with it (e.g. ethylene, propylene, styrene, methyl methacrylate, or vinyl chloride). There are then two possibilities for biphasic processing.

In *suspension polymerization*, a monomer–water mixture is vigorously stirred to break up the monomer phase into small, 0.1–5 mm-sized droplets. With monomer-soluble initiators, polymerization begins within the droplets and proceeds as in the bulk without raising heat-dissipation problems thanks to the small volume of the droplets. Since the polymer particles are not stabilized, they usually sediment when stirring is stopped and can then be easily removed. The process is frequently used for the production of poly(vinyl chloride) (PVC), sometimes called S-PVC, and poly(tetrafluoroethylene).

In *emulsion polymerization*, the initiator needs to be soluble in water. A surfactant or protective colloid is added to produce an enormous number ($\sim 10^{21}$) of 4–5 nm micelles and a much lower number ($\sim 10^{14}$) of 1 μm monomer droplets. The latter act as reservoirs from which polymerization is fed “on demand” as the reaction progresses. Initiation occurs in the aqueous phase, from which the growing chains migrate almost exclusively into the micelles whose number overwhelms that of the monomer droplets. For the same reason, the likelihood of two growing chains migrating into the same droplet is rather low, so bimolecular termination within the droplets is quite rare. As a result, polymers prepared by emulsion polymerization can have unusually high molecular weights. The final surfactant-stabilized polymer emulsion is called latex and is frequently sold as is as a basis, for instance, for paints.

4 The Solid State

4.1 The Glass Transition

The long chains of polymers with their vast number of conformations and broad distribution of chain lengths generally make crystallization difficult. For amorphous polymers, the glass transition is the only transformation through which changes in mechanical properties have important implications in that T_g marks either the upper service temperature for amorphous thermoplastics or, in contrast, the lower one for elastomers.

In polymer chemistry, the glass transition temperature is defined as the onset of large-scale cooperative motion

of chain segments [12]. A number of kinetic or equilibrium theories have been developed to account for the glass transition and the factors that influence it. The most widely used is the free-volume theory of Williams, Landel, and Ferry [13]. Actually the free volume V_f is not the unoccupied space that is inevitably left in an ordered or random packing of molecules. It is rather the space additionally occupied by molecules as a result of their thermal motion [9], whose amplitude increases with temperature as related to the coefficient of thermal expansion. For most amorphous polymers, the free-volume fraction $V_f/\bar{V}$, where $\bar{V}$ is the specific volume, has a constant value of 0.025 [12] when a glass forms upon cooling at the universal viscosity of 10^{12} Pa.s (Chapter 4.1). In other words, this fraction is the limit at which the large-scale cooperative motion of chain segments sets in upon heating or subsides upon cooling.

4.2 Structural Control of the Glass Transition

In light of the relation between T_g and molecular motion within the chain, it is evident that all factors influencing the mobility also influence T_g . The most important are (i) molecular weight; (ii) chain flexibility; (iii) geometric factors along the chain such as symmetry, branching, and side chains; (iv) attractive forces between chains such as polarity, cross-linking, and crystallinity; and (v) external factors such as plasticization, pressure, and rate of testing.

A simple example is the increase of T_g with molecular weight. Since they are only bound only on one side, chain ends are more mobile than internal chain segments and, thus, contribute more to the free volume. As the molecular weight decreases for a given polymer, the ratio of chain ends to internal segments increases, which results in a lower T_g . The effect is stronger at lower molecular weights, however, so T_g ultimately reaches an upper limit. Fox and Flory relied on such considerations to obtain the following equation:

$$T_g = T_g^\infty - \frac{K}{\bar{M}_n}, \quad (7)$$

where T_g^∞ is the glass transition temperature of chains of infinite length in Kelvin and K is a constant related to the free volume [14, 15]. For poly(styrene) (PS), the values $T_g^\infty = 373$ K and $K = 2 \times 10^5$ K g/mol have been found [12]. In light of Eq. (7), the T_g data presented in Table 1 can only be seen as guides. Some of discrepant T_g values reported in the literature might actually result from disregard of the actual molecular weights and the structure of the polymers.

Another effect on T_g is that of chain flexibility, which correlates with the rotational barrier about covalent

Table 4 Influence of chain flexibility on T_g [3].

Polymer	T_g (°C)
$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---O---} \\ \\ \text{CH}_3 \end{array} \right]_n$	-123
$\left[\text{CH}_2\text{---CH}_2 \right]_n$	-78
$\left[\text{---} \langle \text{C}_6\text{H}_4 \rangle \text{---O---} \langle \text{C}_6\text{H}_4 \rangle \text{---SO}_2 \text{---} \right]_n$	250

bonds in the polymer backbone, in particular with the energy differences between the rotational isomers of *gauche* and *trans* conformations. This effect is particularly pronounced in poly(dimethylsiloxanes), owing to the large mean Si–O–Si bond angle and broad bond angle distribution of 105–180°, and in poly(ethylene), in view of its slender chain (Table 4). In contrast, aromatic rings in the polymer backbone increase the rotational barrier and give rise to high- T_g materials such as PES.

A more pronounced influence on T_g is exerted by geometric factors along the chain. Symmetry is the simplest of these factors although its effects may be convoluted. The T_g of -10 °C of poly(propylene) $\text{CH}_2=\text{CHCH}_3$ (PP), for instance, compare with the value of -70 °C of poly(*iso*-butylene) $\text{CH}_2=\text{C}(\text{CH}_3)_2$ (PiB). Similar differences are observed for PVC $\text{CH}_2=\text{CHCl}$, $T_g = 98$ °C and poly(1,1-dichloroethylene) $\text{CH}_2=\text{CCl}_2$, $T_g = -18$ °C, as well as for poly(vinyl fluoride) $\text{CH}_2=\text{CHF}$, $T_g = 41$ °C, and poly(1,1-difluoroethylene) $\text{CH}_2=\text{CF}_2$, $T_g = -35$ °C [2]. In these cases, one could surmise that an additional substituent in the chain would increase rotational barriers, and T_g by the presence of more unfavorable *gauche* conformations. But the additional substituent requires first of all more space, thereby forcing the chain to adopt a more open structure, which increases the free volume and results instead in a lower T_g .

The symmetry effect becomes more pronounced as substituents become larger, as in the case of polymers exhibiting branching or side chains. Large, flexible branches that can originate from chain transfer to the polymer during radical polymerizations force the chains further apart, which increases the free volume and lowers T_g . The effect of side chains can be easily observed when comparing a series of methacrylates (Table 5). Aliphatic side chains are rather flexible, so increasing their lengths gives rise to lower glass transition temperatures. In contrast, rigid or bulky substituents such as phenyl groups (C_6H_5) hamper cooperative motion and thus raise T_g .

Table 5 Effect of side chains on T_g for a series of methacrylates [2].

General formula	R	T_g (°C)
$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C} \text{---} \text{C} \text{---} \\ \\ \text{C=O} \\ \\ \text{O} \\ \\ \text{R} \end{array} \right]_n$	CH_3	106
	$(\text{CH}_2)_3\text{CH}_3$	20
	$(\text{CH}_2)_7\text{CH}_3$	-20
	C_6H_5	110

Other complications result from the fact that the free volume claimed by a single chain is not fully determined by the conformations adopted in the course of cooperative motion. The constraints imposed by the neighboring chains must also be taken into account. Chains in close vicinity, for instance, experience attractive forces, which are at least one if not two orders of magnitude weaker than the covalent C–C and C–O bonds that hold together the polymer backbone. Such non-covalent attractive effects may be van der Waals forces (mainly effective in simple polymers such as PE and PP), dipole–dipole interactions, or hydrogen bonding. For high-molecular-weight polymers, attractive forces between chains can act at a large number of positions along the chains. Even though such interactions are individually weak, their sum may be considerable. This *cooperative effect* is, for instance, the reason why polymers decompose on heating under normal conditions before they can separate into individual molecules in the gas phase.

Clearly, all factors that increase attractive forces between chains and impede chain separation cause a reduction of the free volume and an increase in T_g . In the pair PP/PVC, where the steric demand of the substituents are comparable, T_g increases from -10 °C for PP to +87 °C for PVC because of the increased polarization of the C–X (X = CH_3 , Cl) bond. Likewise, in the pair PS/poly(4-vinylpyridine), T_g increases from 95 °C for PS to 142 °C for poly(4-vinylpyridine). Another factor impeding chain separation is cross-linking, i.e. chains covalently bound to one another by short units to form a 3-D network. This factor prevents the chains from moving too far apart and also shortens the flexible parts, since cooperative motion is only possible for segments between the cross-links. For slightly cross-linked systems such as vulcanized rubbers, the empirical correlation

$$T_g = T_g^0 + \frac{3.9 \cdot 10^4}{\overline{M}_c} \quad (8)$$

has been found [12], where T_g^0 is the glass transition temperature of the non-cross-linked polymer in K and $\overline{M}_c$ is the number average molecular weight between the

cross-links. Although only properly applicable to low cross-linking densities, Eq. (8) would clearly yield irrelevant T_g values as the chain length between the cross-links gets smaller. This is indeed observed in highly cross-linked systems such as epoxies, for which no T_g can be detected.

4.3 Semicrystalline Polymers

The preceding discussion applies only to fully amorphous polymers. For example, straight-chain aliphatic substituents remain so up to a length of about 14 carbon atoms. Longer chains tend to crystallize [16] because the enthalpy released when crystalline domains form in side chains overcomes the entropic effects of conformational freedom of the backbone. In addition, crystallization increases the intermolecular attractive forces, which in total retards the onset of cooperative motion [16].

In semicrystalline polymers, crystalline domains act as physical cross-links with the same effect on T_g as covalent cross-links. Semicrystalline polymers additionally exhibit a melting temperature T_m , which thus marks their upper service temperature. It turns out that some of the factors influencing T_g such as intermolecular attractive forces also affect T_m in the same direction. There is to date no known physical correlation between T_g and T_m , which seems unlikely to exist since melting is a true first-order transition, whereas the glass transition is not. However, when plotting T_g vs T_m , most linear homopolymers are found between a ratio $T_g/T_m = 0.5 \dots 0.8$ (Figure 11). That is, when using one of the above mechanisms to tune the T_g of a polymer, T_m is most likely also altered in the same direction, giving rise to either high $T_g - T_m$ materials or low $T_g - T_m$ materials [11]. One way to gain independent control over T_g and T_m is copolymerization.

4.4 Plasticization

Finally, an industrially rather important concept for lowering T_g is plasticization. The most prominent example is PVC, which turns from a hard, brittle material into artificial leather upon addition of up to 40 wt % of plasticizers. Plasticizers are usually high-boiling, low-molecular-weight liquids such as bis(2-ethylhexyl) phthalate (DOP), which are miscible with the polymer, although short-chain oligomers have been used to reduce migration of the plasticizer [17]. The plasticizing effect can be described in a number of ways: the plasticizer can be seen as a solvent, which separates the chains and reduces the intermolecular attractive forces – similar to the action of the monomer in bulk polymerization. Alternatively, the mixture of polymer and plasticizer can be seen as a blend, for which the T_g can be estimated in a first approximation by Fox' additivity rule:

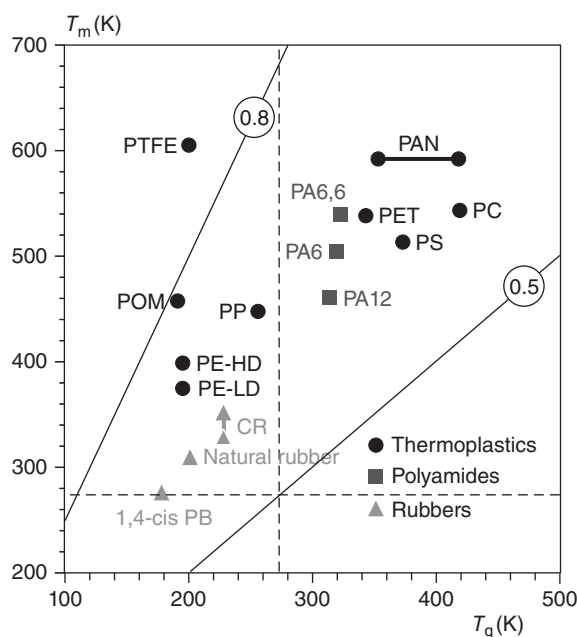


Figure 11 Relation between T_g and T_m for selected polymers, most linear homopolymers having a ratio T_g/T_m ranging from 0.5 to 0.8. Source: Data from Table 1 and [2]. Rubbers unvulcanized. The dashed lines: 0 °C.

$$\frac{1}{T_{g,m}} = \frac{w}{T_g} + \frac{w_1}{T_{g,l}}, \quad (9)$$

where $T_{g,m}$ and $T_{g,l}$ are the glass transition temperatures of the mixture and the plasticizer in K and w , w_1 are the weight fractions of the polymer and the plasticizer. A practical example of reversible plasticization are non-iron shirts made from nylon (PA6,6) for which the considerable amount of water taken up during washing lowers T_g below ambient temperature. When hung up wet, the weight stretches the fibers and removes creases. During drying, the T_g shifts back to higher temperatures and fixes the smooth appearance.

5 Perspectives

Compared with wood, bricks, alloys, and mortar, polymers are rather young engineering materials. Since the beginning of their large-scale industrial production and widespread use in the 1950s, polymer chemistry and processing has improved tremendously. A number of teething problems such as poor impact resistance and weathering properties can today be properly dealt with. However, all commodity polymers and virtually all high-performance materials are oil based. Currently, about 6% of the world oil production is used for the chemical product tree, among which monomers are only one

branch. If light crude oil were becoming increasingly scarce, a political and social decision would then be necessary on whether most of the produced oil simply be burned or rather transformed into value-added products.

Independently of when is raised and how it will be solved, the future will see a significantly increased focus on polymers from renewable resources having full biodegradability. Here, two aspects will be important: (i) substituting commodity polymers such as PE and PP by materials with appropriate properties and made from renewable resources that are available in sufficient quantities and (ii) finding substitutes for engineering polymers, in particular the polyamide and polyester families. An example that is already well on track is poly(lactic acid) (PLA), with a current annual production of approximately 150–200 kt, for instance, used for packaging. However, promising substitutes for important families such as polyamides have yet to come.

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8.9

Hybrid Inorganic–Organic Polymers

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1 Introduction

Nowadays, glasses and polymers are materials that have found widespread applications in nearly all aspects of our daily life. Very early on, scientists and engineers have also tried to design composite materials, such as fiber-reinforced polymers, which combine specific properties of glasses and organic polymers to fulfill requirements that could not be met by a single class of products. But these materials are macroscopically heterogeneous because the glass and polymer phases remain distinct. Further advances to achieve unique properties would require to integrate homogeneously, at the atomic level, two different phases, be they polymer, glass, ceramics, or metal, to form real *hybrid* materials in the same sense as hybrid animals or plants are crossbred from different species [1, 2].

The only means to produce such homogeneous materials from a priori incompatible elements of course rely on low-temperature chemical methods using molecular precursors. Various types of hybrid materials obtained in these ways have been described in the literature [3–10], for instance, interpenetrating inorganic and organic networks, organic dyes in inorganic matrices, core-shell organic–inorganic particles, and many others. In the present chapter, we will focus on the combination of inorganic glass-like structures and organic polymers called inorganic–organic polymers (IOP) as synthesized by the sol–gel process. These materials can uniquely combine the properties of glasses (e.g. high transparency, mechanical stability) and organic polymers (e.g. flexibility and workability at lower temperatures as compared with glass-melting processes).

Standard inorganic sol–gel processing (Chapter 8.2) was invented in the midst of twentieth century with the initial goal of preparing glasses and ceramics from liquid precursors [3]. During the late 1970s, this method has been extended to the incorporation of organic network modifiers into an inorganic oxidic network to form the so-called organically modified silicates (Ormocils). In a next step, not only could functionalization of the inorganic network be realized but also the possibility to synthesize additional organic crosslinks/networks between the inorganic units. As will be discussed here, this achievement was the beginning of IOP materials termed ORMOCER®. These are thermosetting materials, so that shaping processes are irreversible upon final curing – an important difference with respect to thermoplastic polymers or inorganic glasses whose shaping can be repeated several times if necessary. Since the variability of organic groups is quite high, a large playground for the synthetic chemist and material scientist opened up, leading to interesting applications in the field of coatings, bulk materials, fibers, and composites [5, 7, 8]. A small selection will be described in this contribution.

2 Sol–Gel for Hybrid Materials

2.1 Precursors, Chemistry, and Processing

Because the basic principles of sol–gel processing need not be described again (see Chapter 8.2), we will focus instead on special features relevant for IOPs. In contrast to pure inorganic sol–gel materials, IOPs have organic functionalities connected to the inorganic network and, often, also an organic crosslinking/network connected to the oxidic structures. Although not all of them are present in real IOP, possible structural units are summarized in Figure 1 to illustrate the basic principles at work.

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Based on these structural elements, materials ranging from highly inorganic to pure organic in nature – as well as intermediate hybrids – can be synthesized.

To various degrees, the inorganic silica network can be modified by heterometal oxidic structures $M-O-Si$ ($M = Al, Ti, Zr, Sn$) as well by nonreactive organic groups (R). One organic group per Si-atom opens the inorganic network to a certain extent, sometimes creating porosity in the materials; if two organic groups are introduced at the same Si atom, the inorganic network is drastically modified, evolving toward linear networks of silicone-type structures.

The inorganic network can become connected through introduction of reactive organic groups, forming interpenetrating networks. If the organic connection is short, one obtains hard, elastic materials whereas more flexible ones are generated when the spacer length is long. The spacers can be further modified with functional groups that, for instance, yield special adhesion properties on various surfaces. If even more organic structures are connected to the hybrid network, the material becomes more akin to an inorganically modified organic polymer, which can be of practical interest when a bulk material with a high mechanical flexibility is required.

Actually there exists a complete spectrum between purely inorganic and organic polymer networks depending on which precursor is used among the four main

different types that have been defined (Figure 1). In practice, one can achieve highly interesting combinations of properties just by choosing the appropriate precursor that will generate the desired structural unit. Metal alkoxides ($Si-, Al-, Ti-...$) are, for instance, used when a purely inorganic network is to be built (type-I precursors) whereas modifications of an inorganic network are based on type-II precursors with hydrolytically stable $Si-C$ bonds (see Figure 2).

With type-III precursors, one forms organic crosslinks/networks between inorganic units by reaction of Si-bonded (meth)-acrylic or epoxy groups. Also mercapto-/vinylalkoxysilane reactions are often used, especially in UV-curable systems. They lead to short organic chain crosslinks between the inorganic units avoiding at the same time the use of UV-initiators.

If type-IV purely organic monomers are used (e.g. acrylates), copolymerization with the organic reactive groups of type-III precursors can occur, which extends the character of the IOP even more toward that of organic polymers. Some influences of the modification of the basic $Si-O-Si$ network on the properties of materials are shown in Figure 3.

Flexibility/elasticity is mainly determined by the amount of pure organic structural units or organic crosslinks with long spacer groups. The nonreactive functionalization is very often used to control the polarity

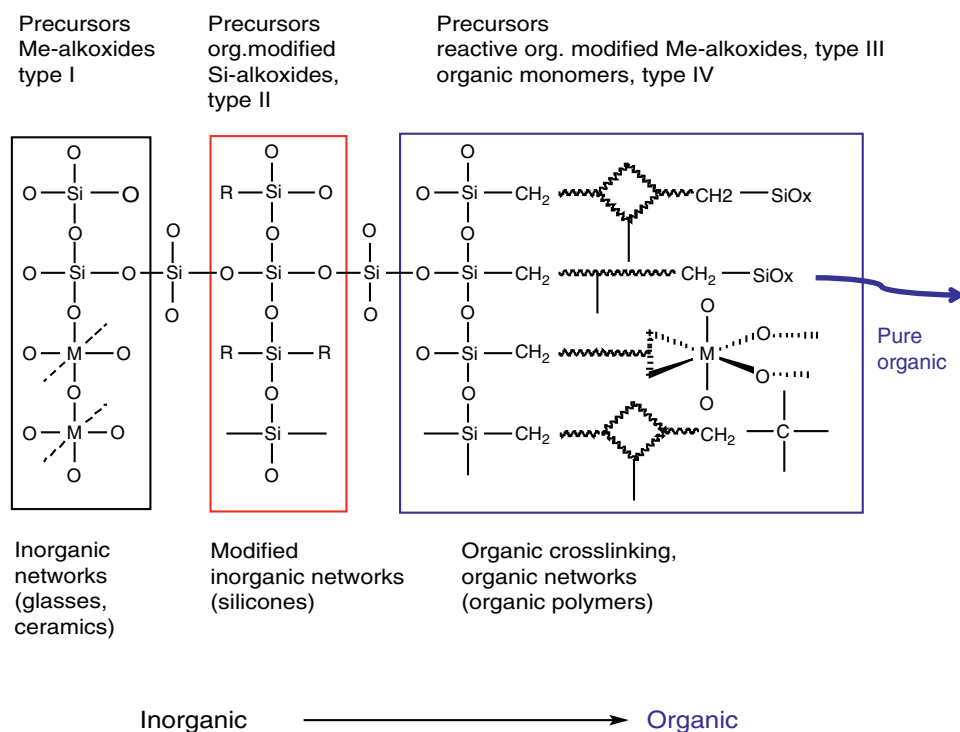


Figure 1 Structure of glasses, silicones, and organic polymers, which can be synthesized using specific precursors (type I–III shown in Figure 2) leading to hybrid inorganic–organic polymers.

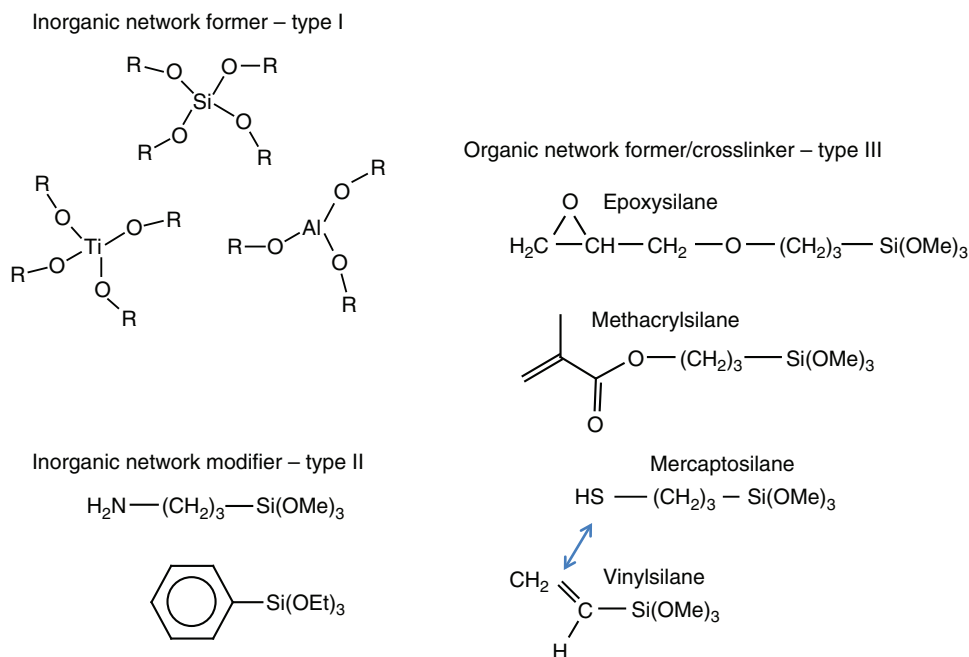


Figure 2 Examples of different precursor types (I–III) for sol–gel/hybrid materials forming inorganic, organic networks, or for modifying the inorganic network; beside Si-alkoxides also other metal alkoxides can form inorganic networks.

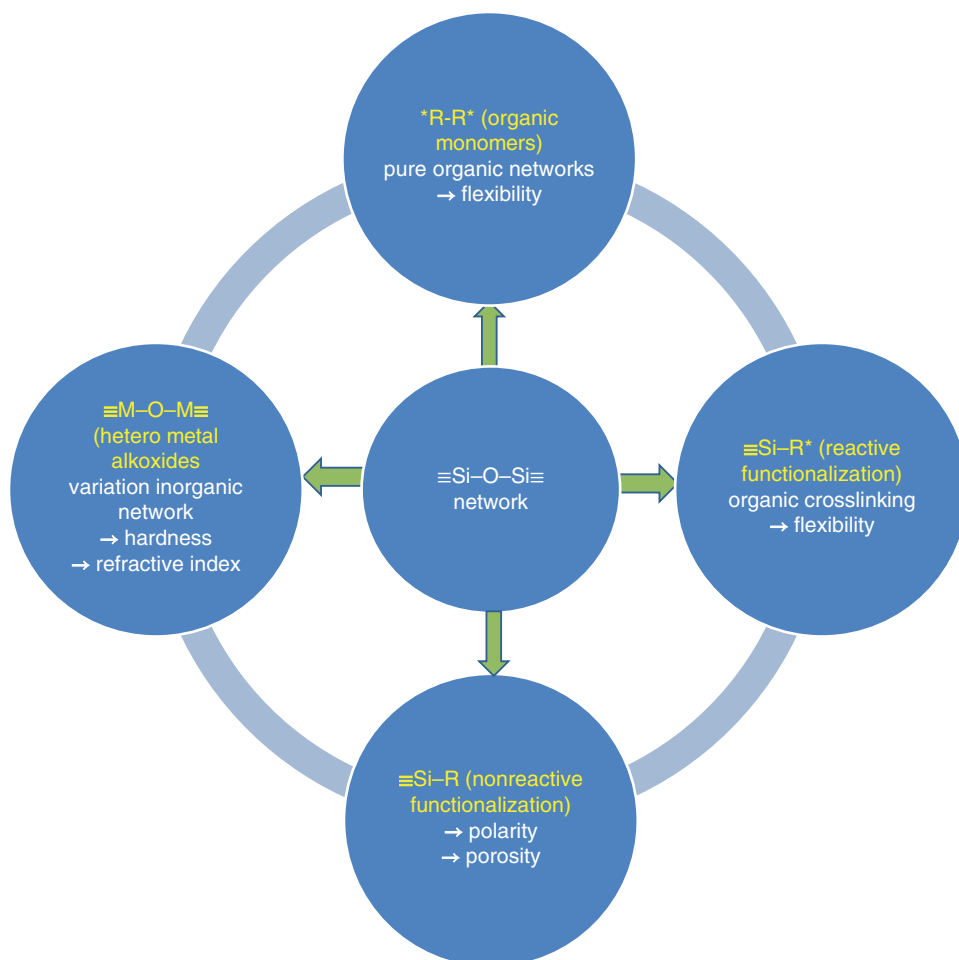


Figure 3 Resulting properties of IOP by the modification of $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ network by heterometal elements, organic monomers, nonreactive and reactive functionalization.

(hydrophilic/hydrophobic), to generate special functions like antistatic or antimicrobial properties, or even to synthesize porous materials when mainly inorganic sol–gel networks are formed. Substitution of Si in the network by other elements (i.e. Ti-, Zr-, Al-, Sn-, or others) can increase the hardness of the hybrid network and allow the refractive index to be controlled. The reactivity of these hetero-metal alkoxides in the hydrolysis step is quite high compared with that of other reacting organically modified Si-alkoxides. Hence, modification of metal alkoxides (chelates, complex formation, etc.) is necessary to slow down their reactivity and guarantee a homogeneous material at a molecular level.

The processes leading to IOP usually require two steps, the first being the hydrolysis and polycondensation

First step: formation of inorganic network

Hydrolysis



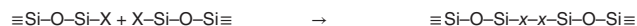
Polycondensation



(possible cocondensation with other metal alkoxides –Ti, Al, Zr...)

Second step: formation of organic network/crosslinking

Crosslinking of Si-bound monomers,
copolymerization with non-Si-bound organic monomers also possible



X: (meth)acrylics, epoxy, vinyl, isocyanate...

Curing: thermal, UV, Redox, plasma

Figure 4 Two-step formation reactions of inorganic and organic networks of inorganic–organic polymers.

reactions as in the case of pure inorganic materials (Figure 4). This first step runs at low to medium temperatures in solution (i.e. below 100 °C) and results in organically modified $\equiv\text{Si}-\text{O}-\text{Si} \equiv$ clusters in a liquid dispersion, the sol. The hydrolysis and condensation reactions themselves are pH-sensitive, so that in many cases the pH has to be adjusted to acid or alkaline conditions. As described in Chapter 8.2, pure metal alkoxides are not miscible with water so that a common solvent – often alcohols – is used as a starting homogeneous solution. The resulting sol/resin can then be processed as in classical sol–gel processing to yield particles, coatings, fibers, or bulk materials. After the shaping step, one finally cures the materials to complete the inorganic network forming reactions and build the organic network/crosslinking (second step in the reaction) by heating of the samples at up to 200 °C, by UV irradiation or even by atmospheric plasma treatment in nitrogen [11].

Radical initiators are used for UV-curing whose advantages are to be very fast and energy efficient. In some cases, oxygen inhibition of the radical polymerization reaction has to be prevented through a nitrogen purge. Since vinyl-/mercaptopalkoxysilane reactive systems can often be used without UV-initiator, they are very favorable in biomedical applications or for coatings with possible food contact. Owing to mild curing conditions, the organic functionalities remain in the IOP in which they ensure its desired properties and, in addition, allow thermally sensitive substrates like some polymers or even paper to be coated.

The formation of monolithic bulk materials or thick films of IOP can often be achieved without having to deal with shrinking processes during gel drying (see Section 4). A comparison between inorganic and hybrid sol–gel processing is shown in Table 1.

Table 1 Comparison of inorganic and hybrid sol–gel processes/materials (common sol–gel properties excluded, see Chapter 8.2).

	Advantage	Disadvantages
Inorganic	• Low-cost precursors • Temperature stability • Porous materials are easily achievable	• Risk of cracking • Bulk materials not easily achievable • Thermal treatment for sintering or crystallization needed • Organic functions can be introduced only through post processing
Hybrid	• Organic groups offer great functionalities when covalently bonded to network (stability) • Controlled polarity of surfaces • Soft processing conditions (temperature, UV) • Fast UV processing possible • Bulk materials achievable without cracking	• Precursors more expensive • Temperature stability limited due to organic functions • Crystallization of inorganic compounds often not possible due to temperature restraints

2.2 Overview of IOP Properties

As described in Section 2.1, the resulting properties of IOPs are determined by the basic structural units, which belong either to inorganic glasses or organic polymers. A comparison with various material classes made in terms of an Ashby plot [12] for the density–Young’s modulus relationship show that – as far as mechanical stiffness is concerned – the IOPs discussed in this contribution are more akin to reinforced organic polymers than to typical glasses or ceramics (Figure 5).

Many physical properties of IOPs that can be tailored through a combination of basic structural units are summarized in Table 2. In view of the higher atomic weights of the inorganic components, the density of IOPs is slightly higher than that of usual organic polymers. The thermal stability is mainly limited by the nature of the organic groups in the hybrid network, which makes these properties similar to those of organic polymers. Their mechanical properties (stiffness) range from very soft up to very hard depending on the amount of inorganic and organic domains, and especially on the spacer length between the crosslinked inorganic clusters. Since IOPs are homogeneous materials on a molecular scale, high transparency and low optical losses make them very well suited for optical applications (e.g. optical waveguides, micro optical components, fiber optical coatings, and sensors).

The electrical properties are tuned by the functionalization of the organic network from pure insulators/dielectrics up to ion-conducting polymers. The

Table 2 Overview of properties of hybrid polymers.

Property	Typical range of values	Comments
Density	1.1–1.6 g/cm ³	Without fillers
Thermal expansion coefficient	50–200 ppm/K 18–70 ppm/K	Without filler With filler
Thermal stability	180–400 °C	Less than 5 wt % loss (TGA)
Stiffness	0.0013 GPa up to 18.6 GPa	High organic content High inorganic content
Refractive index (at optical wavelengths)	1.42–1.62	Without fillers
Optical losses (1310, 1550 nm) (633 nm)	≥0.3 dB/cm ≥0.06 dB/cm	Not fluorinated
Electrical resistance	10 ¹⁶ Ω cm 10 ⁸ Ω cm 10 ³ Ω cm	Passivation Antistatic Ion conductors (H ⁺ /Li ⁺)
Dielectric number	≥3.2 at 10 kHz	Coatings
Dielectric losses	≥4·10 ^{−3} at 10 MHz	Coatings
Dielectric strength	100–400 V/μm	Coatings
Permeability for oxygen	From less than 10 up to 130,000 cm ³ /m ² d bar	Ideal for barrier coatings or contact lens materials or nonporous membranes

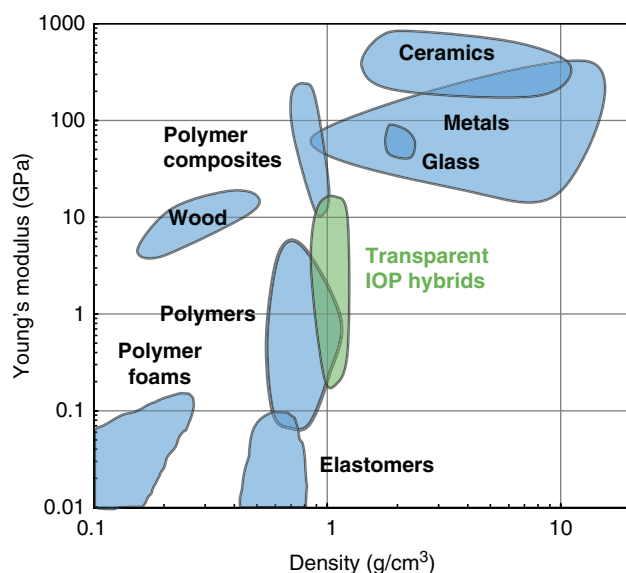


Figure 5 Ashby plot for the Young’s modulus–density relationship of various material classes and comparisons with transparent hybrid inorganic–organic polymers.

influence of the inorganic and organic network density is especially prominent regarding the permeability to gases. Highly permeable IOPs have open flexible organic networks [13], whereas barrier coatings based on IOPs show high condensation degrees and network densities [14].

3 Coatings

3.1 Capillary Forces and Precursors

The production of glasses and other inorganic bulk materials via sol–gel processing is more or less limited by the capillary forces that act during drying and result in important shrinkage (Chapter 8.2). To overcome this significant obstacle, supercritical drying is applied in the manufacturing of ultralow density materials (aerogels), which function as high-performance insulating materials and, therefore, require larger dimensions ranging

from mm to cm), since the insulating efficiency depends on the volume. Despite their extraordinary properties, the market penetration still remains low because of the high cost of such manufacturing processes (Chapter 8.3).

In contrast, thin sol–gel-derived coatings – either inorganic or hybrid – offer a chance to improve the surface quality of many products without major rise of their cost. Capillary forces upon drying are then fairly limited, thanks to a low thickness in the nm to μm range, which reduces the risk of cracking. This is the reason why careful investigations are made worldwide to arrive at cost-effective manufacturing processes for high added-value coatings on goods requiring high surface quality and environmental stability.

The most important precursors used in sol–gel processes are silicon compounds, namely alkoxysilanes and organo(alkoxy)silanes, potentially combined with main group or transition metal alkoxides. Their hydrolysis and condensation reactions initiated during sol–gel processing are well known as they have been extensively studied by various research teams. As silanol groups are formed by hydrolytic reactions of alkoxysilanes and organo(alkoxy)silanes, the protection and functionalization of glasses also exhibiting silanol groups on their surfaces has been the focus of early studies concerning the application of sol–gel-based coatings.

3.2 Coatings on Glass Surfaces

The corrosion of historic glasses through the formation of gel layers due to ion-exchange processes is a well-known phenomenon studied in detail by researchers in the field of cultural heritage preservation [15]. Because of inadequate chemical compositions (Chapter 10.8), many historic glasses are more prone to leaching than modern glasses. To reduce the potential damage of environmental factors, such as moisture and atmospheric pollutants on those highly valuable artworks, special coatings have been developed and applied on several historical sites throughout Europe.

In the case study of the Herrgottskirche in Creglingen (Germany), a coating generated by cohydrolysis of tetra-ethoxysilane (TEOS), diphenyl-diethoxysilane (DPDEOS) and methyl-vinyl-diethoxysilane (MVDEOS) has been applied on the exterior side of a stained-glass window from the thirteenth century exhibiting severe glass corrosion (Figure 6). The coating was applied in a workshop after de-installation and careful cleaning of the glass piece in 1988 and reinstalled afterward. In 2010, the condition of the coating has been assessed while scaffolding was available to renovate the stone facade. The condition of the coated glass surface has been

(a)



(b)



(c)



Figure 6 Conservation of a historic glass window at the Herrgottskirche (Creglingen, Baden-Württemberg, Germany). (a) Interior view; (b) exterior view; (c) detailed view of glass pieces coated in 1988 with ORMOCER G, a condensate derived from tetra-ethoxysilane, diphenyl-dichloro-silane, and methyl-vinyl-dichloro-silane. *Source:* Courtesy Paul Bellendorf.

documented and photographed and a very small sample of the coating material removed. After these 22 years of exposure to sunlight, rain, and atmospheric pollutants

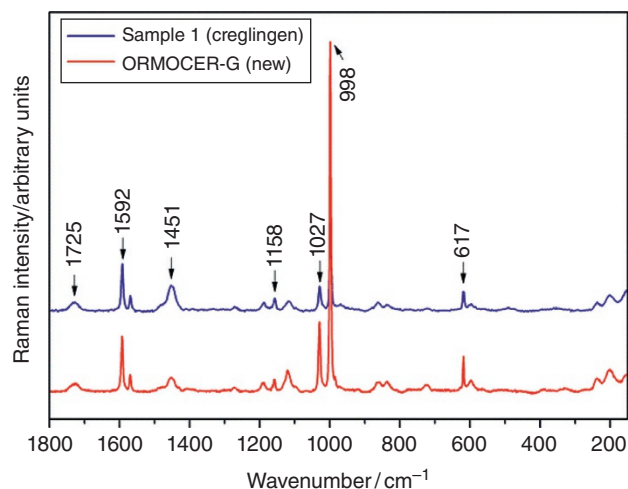


Figure 7 Micro-Raman spectra of exposed coating material (top curve) and freshly prepared reference sample (bottom curve). Main band assignments: $\nu(\text{C}=\text{C})$: 1592 cm^{-1} , $\delta(\text{CH}_3)$: 1451 cm^{-1} (br), $B_1\nu_{17}(\text{aryl})$: 1158 cm^{-1} ; $A_1\nu_{14}(\text{aryl})$: 1027 cm^{-1} ; $A_1\nu_6(\text{aryl})$: 998 cm^{-1} ; $B_1\nu_{18}(\text{aryl})$: 617 cm^{-1} .

(as the church is located close to a road), it turned out that the coating still adhered very well to the glass and exhibited no delamination, cracking, or other degradation phenomena.

The small coating sample taken from the surface of the glass has been analyzed by Micro-Raman spectroscopy and compared with a freshly prepared reference sample. Both spectra are identical (Figure 7); therefore, the environmental stability of this ORMOCER[®]-coating material seems to be fairly high, at least on this timescale. The composition of the coating had been designed to ensure high light stability, water repellence, optical transparency, and reversibility as it can be removed by dissolution in organic solvents (e.g. ethyl acetoacetate) to meet the standards of cultural-heritage preservation.

Concurrently, similar types of protective or decorative coatings for crystal glasses have been designed through combination of 3-glycidoxypropyl-trimethoxysilane (GPTMS), aluminum alkoxides, and organic prepolymers (epoxy resins) through cohydrolysis and cocondensation. Dip-, spray-, or spin coating procedures followed by thermal curing around $100\text{--}200\text{ }^\circ\text{C}$ result in highly cross-linked hybrid materials exhibiting thicknesses in the lower micrometer range. High abrasion resistance, optimal adhesion, simple colorability by incorporation of either organic dyes or inorganic pigments, and high gloss are achieved through these simple manufacturing procedures. The integration of organic constituents has been decisive to achieve high chemical stability, especially for glassware frequently subjected to dishwashing at high pH-values [5].



Figure 8 Low-energy hybrid polymer coating on glass: liquid droplet on the rim of a glass container easily removed, leaving little chances to spoil the surroundings.

Owing to the intricate hybrid network structure of these IOPs, the potential for migration of ions or molecules through this network is very low so that a high chemical stability can be expected. For high-lead crystal glasses, the leaching of lead ions is largely suppressed and, therefore, the coatings may be used as barrier films on glass surfaces [5]. At the same time, leaching of the individual constituents of the coating is also minimal and allows to meet FDA regulations for uses as drinking glasses or food containers.

The surface modification of glasses is useful to prevent not only the migration of small chemical entities out of the bulk material, but also to repel chemicals from migrating to the glass surface and wetting it. One best achieves this feature by designing hydrophobic and oleophobic coatings, which contain long alkyl chains or perfluorinated alkyl chains connected to the silica/silicone backbone. The high efficiency of these coatings originates in the separation of the long alkyl chains from the more polar parts of the sol-gel-based network (silanol groups and polyether chains). The nonpolar chains then find themselves enriched at the surface of the cured coatings and lower their surface free energy, as also achieved with perfluorinated organic polymers (e.g. Teflon[®]). With these coatings, special types of commercial crystal glass vessels are treated on the top rim to avoid droplets from adhering to the glass and rolling down on its external side (see Figure 8). Only a very thin layer (well below $1\text{ }\mu\text{m}$) is needed to change completely the wettability of the glass so that several hundred thousand glass vessels can be coated with 1 l of the coating solution. The coating process is a simple manual treatment using a sponge-type material.

3.3 Coatings on Metals and Polymers, UV- and Plasma Curing Techniques

Very often IOP compositions that are used as glass coatings are also applicable on various metal surfaces like Cu, Al, or steel to generate dense layers for corrosion protection or also as low surface free energy (“easy-to-clean”) coatings mainly based on precursors that are cured thermally (III.2 in Table 1) and are combined with perfluorinated alkylalkoxysilanes. Such an example of IOP coating on copper metal is shown in Figure 9.

A second type of precursor generating hybrid networks is 3-methacryloxypropyl-trimethoxysilane (MPTMS), which after hydrolysis enables the formulation of UV-curable IOPs [5]. This compound requires the addition of photo initiators in substantial amounts to trigger the photopolymerization of the acrylic groups. But the cohydrolysis and cocondensation of precursors such as vinyl-trialkoxysilanes and thio-substituted alkoxysilanes leads to IOPs’ crosslinking under UV irradiation without any photo initiator. Both reaction schemes require curing times of only a few minutes. They have been used to formulate scratch- and abrasion-resistant coatings on plastics [16]. The synthesis of silanes equipped with several acrylic substituents per one silicon atom (see e.g. Figure 10) has been performed to realize ultrafast curable coatings for glass fibers used in telecommunication [17] as well as in sensing devices (Chapter 6.4). The copolymerization of selected monomers enables application-oriented tailoring of properties like hardness, flexibility, refractive index, transparency, adhesion, and curing speed. The resulting tunable resins are especially useful to replace organic coatings in optical glass-fiber manufacturing because of their superior adhesion and mechanical performance. More recently, protective coatings for fiber

Bragg grating sensors have become a commercially available product offered by FBGS company in Jena, Germany.

An interesting optical application of micro/nanostructured IOPs has been made possible by embossing techniques. The so-called “moth-eye” patterns can be created to realize antireflective surfaces both on plastics and glass [18]. The patterning process is based on a two-step coating and curing scheme applicable through physical drying of the IOP resin and UV-curing after or during the embossing process. The sub-micrometer structures exhibit dimensions (width and depth) in the range of several hundred nanometers and, therefore, are not visible. Embossing is made possible since the IOP-resin shows high plasticity before curing. In addition, wetting can also

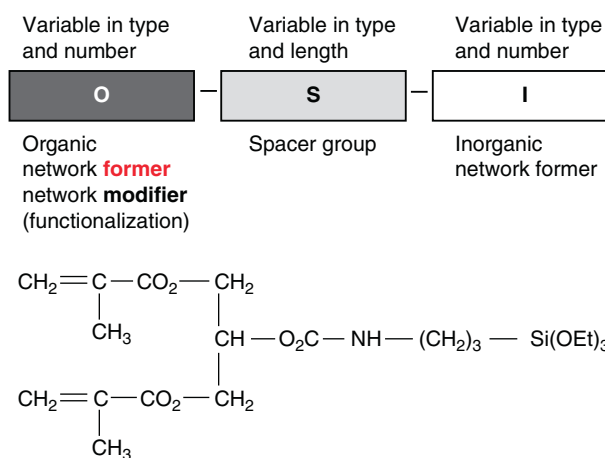


Figure 10 Bifunctional precursors for inorganic–organic polymer designed for bulk materials and composites and their role in network formation/connection, including an example for dimethacrylic silane.



Figure 9 Corrosion protection through hybrid polymer on copper substrates: left side, uncoated; right side, coated.

be controlled by the microstructure depending on the hydrophobic or oleophobic nature of the IOP. In the former case, the wetting angle of water on polymer or window glass substrates, for instance, may increase from around 105° for unstructured to above 140° for microstructured surfaces. This is an example of the well-known *lotus-leaf* effect.

In usual sol–gel processing, the wet-chemically deposited coatings are either cured thermally or by UV irradiation. In the last decade, however, alternative techniques like plasma processes or electron-beam curing have allowed novel properties of the final coating to be obtained.

Plasma exposure of coatings or plasma depositions of aerosol particles with metal alkoxides or prehydrolyzed sols have, for instance, proven to be feasible on glass or plastic substrates [11]. As an example, such a coating on a silicon substrate based on epoxysilane deposited with an atmospheric plasma (nitrogen-purge) can be thinner than 200 nm (Figure 11), which is up to 10 times thinner than achieved with usual wet-chemical coating and curing methods. An interesting point is that these coatings additionally show excellent adhesion to various surfaces – also resulting from the plasma pretreatment – and form very dense networks. These features are of course important in barrier applications or for corrosion protection. Since plasma treatment/curing processes lend themselves to continuous operations, they make some

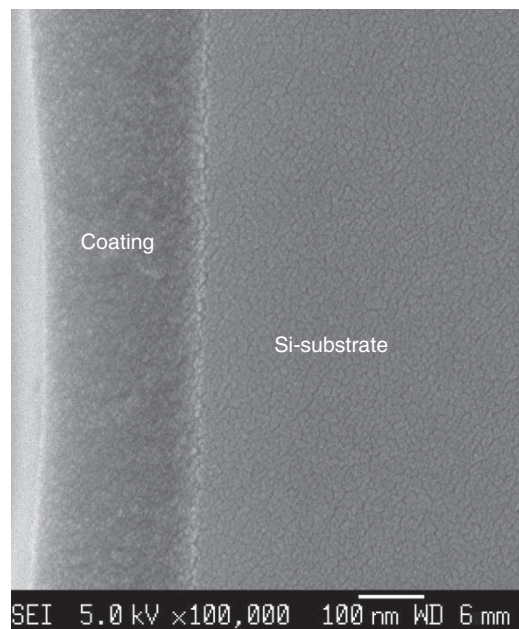


Figure 11 Scanning electron micrograph of a plasma-deposited inorganic–organic polymer coating (epoxysilane-based, left side) on silicon substrate (right side), [11] with kind permission of VITO NV (Belgium).

IOP compositions also relevant to roll-to-roll techniques (R2R) whereby a flexible material on a roll is re-reeled after coating, a process that is becoming more and more important in sol–gel technology.

4 Particles

Other interesting applications of IOPs are (nano)-particles. Various morphologies and synthetic strategies are used in this field as recently reviewed [19]. One strategy is the attachment of ex-situ preformed components (e.g. nanoparticles to polymers, synthesis of polymers around nanoparticles). Others are the in-situ production of inorganic components in the presence of polymers, or a complete in-situ strategy where both components are reacted to form hybrid polymer systems. The hybrids described in this chapter are mainly of the in-situ type.

During classical sol–gel processing of hybrid polymers, the intermediate sol-state is based on hybrid clusters in a liquid medium. If the solvents are removed and the organic reactions have started, hybrid polymers particles can form, for example, via spray drying.

An interesting kind of hybrid polymer particles are the capsules, for example, used for controlled release systems. In this case, a hybrid polymer resin, mainly based on precursors of the type shown in Figure 10, is forced through a nozzle by a gas stream followed by UV-curing of the resulting hollow capsule. The chemical nature of the capsule material – from more inorganic to more organic (open networks, high flexibility, high gas permeation) – can be chosen in a wide area and different applications can be followed using this strategy [20]. Beside solids, even solutions with high amounts of water can be encapsulated, which is usually not easy to achieve.

5 Bulk Materials, Fibers, and Composites

As mentioned, shrinkage upon curing is often minimized by the flexible organic parts of the IOP network. Therefore, compared with purely inorganic sol–gel materials, IOP bulk materials and composites can be more easily processed. Special precursors such as biacrylate-silanes have been developed (Figure 10). They are used to ensure the possibility of adjusting both the organic network density and the spacer length between the inorganic and organic part of the IOP network.

These precursors are processed like others bifunctional silanes. In contrast to coating applications, however, for producing bulk materials, the IOP oligomers contain little or no solvent so that they can be used as resin (i.e. as 100%

solid systems). After shaping, the oligomers are finally cured either thermally, by UV, or even visible light. The shrinkage upon curing is lower than 10 vol %. This figure is much smaller than for usual organic monomers since the first inorganic polycondensation step has already taken place in solution, so that oligomers react instead of monomers in the final curing step. Besides, no monomers remain in the cured material, which is important for biomedical applications.

Especially based on these favorable properties, composites with IOP matrices have been successfully used in dentistry for more than 15 years, the IOP being cured by visible light after application of the flowable material into the tooth cavity [7, 8]. In dental fillings, the shrinkage is further reduced to only 1.2 vol % by the incorporation of high fractions of inorganic (nano)particle fillers [21]. Such a low value is especially important in dentistry because the presence of voids between the filling and the tooth provides much room for reaction sites where bacteria cause caries.

The possibility of UV curing for the IOP resins is also used to generate hollow fiber membranes with controllable permeability for oxygen and selectivity for various gases [13]. The thermal treatment of the dense hybrid material can result in nanoporous silica membranes with selective gas permeation rates [13].

Compared with classical polymers like PMMA, IOPs combine a high transparency with improved mechanical properties that makes them also useful for micro optical components such as waveguides [7]. These structures can, for instance, be formed with embossing techniques, UV lithography, or even two-photon induced polymerization (2PP). The last technique is an innovative one to

generate micro- to nanosized complex structures that can be applied in optics, microfluidics, and biomedicine [22]. Organic polymerization with 2PP techniques is initiated by an intense femtosecond-laser beam. The hybrid resin is transparent at this wavelength and also at the two-photon-wavelength. In the focal area, a photo initiator adapted to this 2P wavelength triggers the organic-polymerization reaction upon laser irradiation. With a computer-controlled system, the laser beam can be guided to develop micro- and nanostructures down to below 100 nm once solvents have removed the non-polymerized parts as in conventional lithography. Here, IOP resins demonstrate their superiority over purely organic monomers because little polymerization develops outside the laser beam through motion of low molecular-weight oligomers, which ensures very fine and smooth surfaces (Figure 12).

6 Perspectives

The field of hybrid inorganic–organic polymers has grown tremendously since the early 2000s in terms of both fundamental research efforts and product development [9, 11].

This contribution cannot cover all future perspectives, but some aspects might be mentioned. Single-source precursors [23] are developed, which widen the scope of hybrid materials. Polymerization techniques like living-radical polymerization generate very special morphologies including hierarchical structures [24].

Additive manufacturing (AM) methods will increase in importance in the near future, because of the potential

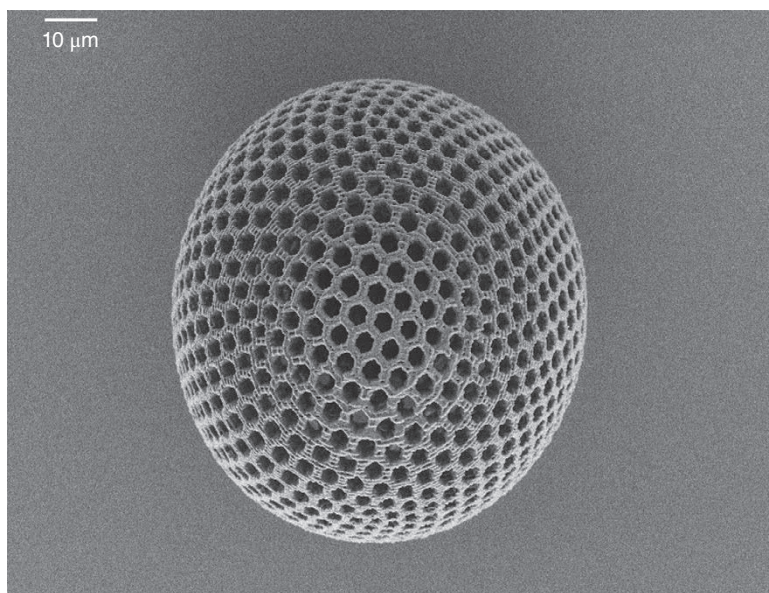


Figure 12 Scanning electron microphotograph of an inorganic–organic polymer structure generated by two-photon-polymerization (stl-File: <http://www.georgehart.com/rp/rp.html>).

they offer regarding special morphologies and individual forms with the possibility to produce individualized products [25]. The 2PP process is one example for an AM method whereas 3-D printing techniques using IOP resins in connection with conventional single-photon absorption by UV light will also be of interest in the coming years.

Biodegradable/-resorbable materials are also highly relevant not only because of environmental issues (stricter environmental regulations) but also for many biomedical applications like implants, tissue engineering, and the like (cf. Chapter 8.4). Here, the incorporation of biodegradable components or even active biomolecules into IOP structures will have much influence on the development of new biomaterials (Chapter 8.4).

Finally, since environmental concerns are becoming an integral aspect of material design and engineering, the question of life-cycle-analysis is also becoming important. Hence, the so-called *green chemistry* approach should and will be applied to existing and newly developed IOPs [2]. In other words, the outstanding features provided by hybrids will certainly lead to new interesting applications in the future and will offer a creative playground for material scientists and chemists alike.

Acknowledgments

This article is dedicated to our colleagues at Fraunhofer ISC, who were involved in the development of IOP in the last three decades.

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Section IX. Environmental and Other Issues



Figure 1 Domestic waste transformed into a piece of abstract glass art: optical micrograph under polarized light of bottom ash from a municipal solid waste incineration plant (Arnoldstein, Austria). Dark glass fraction of about 60% along with skeletal melilite $[(\text{Ca},\text{Na})_2(\text{Mg},\text{Fe},\text{Al})(\text{Al},\text{Si})\text{O}_7]$, plagioclase $[(\text{Na},\text{Ca})(\text{Si},\text{Al})_4\text{O}_8]$, and opaque spinel $[(\text{Mg},\text{Fe},\text{Mn}\dots)(\text{Al},\text{Fe},\text{Cr}\dots)\text{O}_4]$ crystals. Sample width: 3 mm. *Source:* Photo: Soraya Heuss-Aßbichler.

That glass is ubiquitous in the modern world is made most evident by the facades of modern buildings whose glazing controls light and heat interactions with the environment (Chapter 6.8). What is probably less obvious are the technical problems that glass is raising by its brittle nature when used as a structural element in architecture. The various solutions reviewed by F. Bos and C. Louter rely on the use of panels of more resistant laminated or tempered glass, which are connected either mechanically or with adhesives in such ways as to limit the accumulation of stress at places where surface flaws would ultimately result in breakage (Chapter 9.1). Similar problems are faced in the glazing of cars and transportation vehicles in general. As described by R. Gy, laminated and tempered glasses are again used – in proportions that have markedly increased with the complex shapes made possible by modern forming processes – whereas new functionalities are being added to the glass surface in terms of vision, safety, heat, and noise control and even of information display (Chapter 9.2).

In the form of fibers, glass is the prime material for thermal insulation, thanks to its incombustible nature, recyclability, relatively low cost, and to the possibility of engineering its properties for specific uses: whereas *glass wool* optimizes the thermal resistance in terms of thickness, *rock wool* is a unique fire-proof material. Both kinds of fibers are hyperquenched glasses (Chapter 3.8) whose fabrication, properties, and advantages are reviewed by Y. Yue and M. Solvang (Chapter 9.3). Transparency and other traditional properties are also making glass an indispensable active or passive component of all forms of renewable-energy systems described by J. Deubener and G. Hensch, for example, as covers, substrates, or supports for photocatalytic devices (Chapter 9.4). In addition, glass is poised to become a key component in the new generation of all solid-state batteries whose safety will be much increased by the elimination of the current organic liquid electrolytes. Lithium and sodium sulfide glasses are the best potential materials to replace them for the reasons discussed by A. Hayashi and M. Tatsumisago, namely low processability temperatures, high electrical conductivities, wide electrochemical windows, appropriate elastic moduli, and excellent cycle performance (Chapter 9.5).

Closely related to the energy problem is the tremendous growth in glass production in Asia – especially China – during the last few decades, which should also take place in other countries that are developing rapidly. Following a long century of incremental improvements in the production of flat glass, the float-glass revolution of the 1960s not only made this expansion possible but has since then resulted in a continuous decrease in selling costs as explained by B. Savaète (Chapter 9.6).

In spite of rising energy prices, more efficient glass melting furnaces have been one of the factors that have

driven production costs down. Although furnaces belong to only five main types, depending on the energy source, heating systems, and energy recovery via either regenerators or recuperators, C. Jatzwauk explains why each of them must be tailored to specific factors that include the type of production, the intended pull, and the local labor and construction costs (Chapter 9.7). By considering furnaces as chemical reactors and heat exchangers, R. Conradt and E. Muijsenberg then deal with their energy efficiency and describe how this parameter is evaluated and optimized with methods that include finite-element modeling of their design and operation (Chapter 9.8). As already understood and practiced in Antiquity, glass is a material that can be indefinitely recycled. Although it lends itself particularly well to the concept of circular economy and to savings in both energy and raw materials, the practical problems faced by cullet recycling are summarized by S. Ceola and N. Favaro with regard to glass collection, elimination of undesirable impurities, and regular delivery of a material of a quality suitable to the demanding modern glassmaking processes (Chapter 9.9).

The next two chapters deal with glass as a waste-storage matrix. For domestic and industrial waste, aluminosilicate glasses (Figure 1) are major by-products of incineration processes whose main goals are to reduce the volume of the waste to be disposed of in landfills, to eliminate toxic and biological agents, and, possibly, to recover energy. As discussed by S. Heuss-Aßbichler and A.P. Bayuneso in their review of incineration processes, the glasses produced should themselves be stable if disposed of in landfills or as road-base materials, or better, be usable as starting products in the fabrication of cement or ceramic materials (Chapter 9.10).

For radioactive waste, glass is a matrix that, in contrast, has been highly engineered to incorporate in a stable material the elements to be disposed of permanently. Among the matrices discussed by O. Pinet et al. in their worldwide review of vitrification processes and facilities, borosilicates are generally preferred for this application because of the large amounts of foreign elements they can dissolve, their long-term stability ensured by a good resistance to aqueous corrosion, and their low processing temperatures, which make robot-controlled production under highly radioactive conditions less difficult (Chapter 9.11).

To conclude this section, the chapter devoted by J.M. Parker to the International Commission on Glass (ICG) draws attention on the important role that this body has played since its creation in 1933 as a forum for discussing the most pressing technical, scientific, economic, and environmental issues within the glass community at large through its technical committees (24 as of today) and the recognition given by its awards to distinguished glass scientists and technologists (Chapter 9.12).

9.1

Structural Glass in Architecture

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1 Introduction

The diversity of glass applications in construction designated as *Structural Glass* is illustrated by point-fitted glass, glass floors and stairs (Figure 1), or balustrades and façade fins (Figure 2). Glass (roof) beams are becoming more common (Figure 3) whereas glass walls carrying vertical loads or providing lateral stability can be found in a number of projects. Full glass structures with columns, beams, and stability walls all in glass are still rather exotic (Figure 4). In the terminology, it is easy to confuse “Structural Glass” with “Structural Glazing.” The latter, however, specifically refers to glass panels that rely on structural silicone adhesives to connect them to the supporting structure, rather than mechanical fixings. The former has the much broader meaning indicated above.

The history of structural glass is still very young. Although the glass panels used in the conservatories of the nineteenth century often provided stability to the cast-iron structural frames, the current developments can be traced back only to the 1970s. In England, the Willis Faber Dumas building in Ipswich and the Sainsbury Art Centre (Figure 5) in Norwich, both designed by Norman Foster, featured glass fins perpendicular to the glass façade to carry wind loads back to the main structure. The underground extension of the Louvre Museum in Paris featured an early application of glass beams. At the Cité des Sciences et de l’Industrie in the Parc de la Villette in Paris, a façade in which glass panels hanging directly from each other was first constructed (Figure 6). Subsequent milestones included glass half-

portals, a glass footbridge in Rotterdam (Figure 7), a cantilevering glass canopy in Tokyo, several glass staircases, and a free-standing full glass pavilion in Riyadh.

Around the turn of the last century, the development of structural glass gained momentum and the number of projects in which it was used increased exponentially. The extensive use of structural glass by the Apple company in its flagship stores has been an important driving force. The number of research projects at universities focusing on structural glass applications increased accordingly. In spite of growing coverage by codes, education, and research activities, however, it is still a field requiring specific expertise and therefore covered by a relatively limited number of specialist professionals.

This chapter provides an introduction on the issues related to structural design of glass. For further in-depth reading, [2–4] are recommended. Also notable is [5], which provides a thorough introduction into the field, including considerable attention to building physics. In preamble, however, note that structural glass is often part of the building envelope. Considerations of energy performance (most notably thermal insulation and light) are, therefore, often as important as the structural aspects. However, these are beyond the scope of the present chapter.

2 Scheme Design

For a significant part, the schematic structural design of a glass structure is governed, directly or indirectly, by the brittleness of the material (Chapter 3.11). This peculiarity sets it aside from the design of structures made up with other materials such as steel or reinforced concrete and requires specific attention, particularly at the points

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Figure 1 Glass staircase, Apple Store, West 14th Street, New York; Eckersley O'Callaghan. *Source:* Photo courtesy Eckersley O'Callaghan.

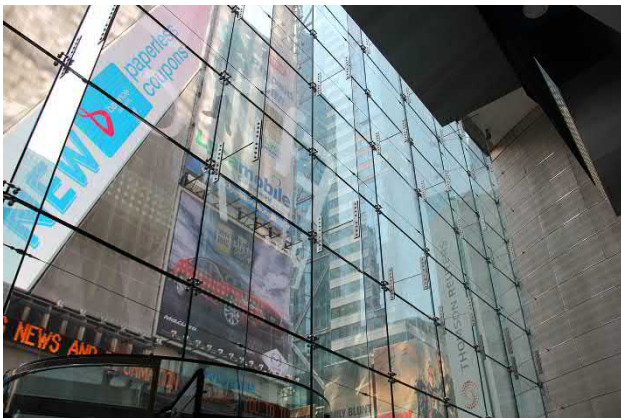


Figure 2 Glass façade with glass fins, Thomson Reuters Building, New York. *Source:* Photo C. Louter.



Figure 3 Glass roof beams, Medical School, Glasgow; ARUP. *Source:* Photo C. Louter.



Figure 4 Full glass structure including columns, beams, and stability walls. Apple Store Cube Mark 2, 5th Avenue, New York; Eckersley O'Callaghan. *Source:* Photo C. Louter.

where stress is exerted on glass pieces. As an example, drilling in the glass causes local damage/defects at the perimeter of the hole, which may significantly lower the local strength. Grinding and polishing of the hole perimeter to remove or at least reduce the defects is, therefore, recommended whenever possible.



Figure 5 Sainsbury Art Centre (Norman Foster). Early example of structural glass wind fins. Source: Photo Nigel Young/Foster + Partners.



Figure 6 Serres of the National Museum of Science, Technology and Industry in the Parc de la Villette in Paris, featuring hanging glass panels. Source: Photo P. Richet.

Brittleness has a number of unfavorable effects on the structural properties of glass [6]. Under increased loading, glass elastically deforms linearly up to failure without providing any warning signal that breakage is imminent. Because peak stresses cannot be redistributed, the strength of an individual piece under a certain loading highly depends on microscopic surface defects, known as Griffith flaws, as well as on possibly present macroscopic accidental flaws (Chapter 3.11).

As a result, the theoretical failure stress of glass, based on the relation between Young's modulus, fracture surface energy, and atom equilibrium spacing [7], is around $32 \cdot 10^3$ MPa, whereas the characteristic bending tensile



Figure 7 Glass foot bridge, Rotterdam, The Netherlands; Kraaijvanger Urbis, ABT/Rob Nijssse [1]. Source: Photo C. Louter.

strength of float glass obtained from practical experience and experimental testing is only 45 MPa. The flaw-governed nature of the failure process also results in a very high scatter in strength test data and in difficulties in predicting the failure load of an individual piece of glass. This is illustrated by test data on glass beams plotted in a Weibull diagram (Figure 8).

Furthermore, since glass has a very low fracture surface energy of $2\text{--}4 \text{ J/m}^2$, it takes little energy for a crack to propagate through the material. As a result, fractures tend to run through a piece of glass completely, and not to remain localized. In addition, Griffith flaws show subcritical crack growth under the influence of tensile stress and humidity (known as static fatigue or stress corrosion), which causes the strength of glass to reduce over time (Chapter 3.11). This feature, too, makes predictions of the strength of an individual element difficult. Combined with the lack of a warning signal before failure and often complete breakage, this calls for specific measures in structural glass design. These concern the following points in particular:

- **Safety:** owing to its material properties, glass is of itself unsafe as a structural material. It lacks robustness and produces very sharp shards that can easily cause injury. Nevertheless, several strategies can be applied to obtain sufficient levels of safety. In the schematic structural glass design, these strategies need to be determined, as further discussed in Section 4.1 of this chapter.
- **Strength:** a range of models have been proposed to describe the strength of glass [10]. In practice, modern

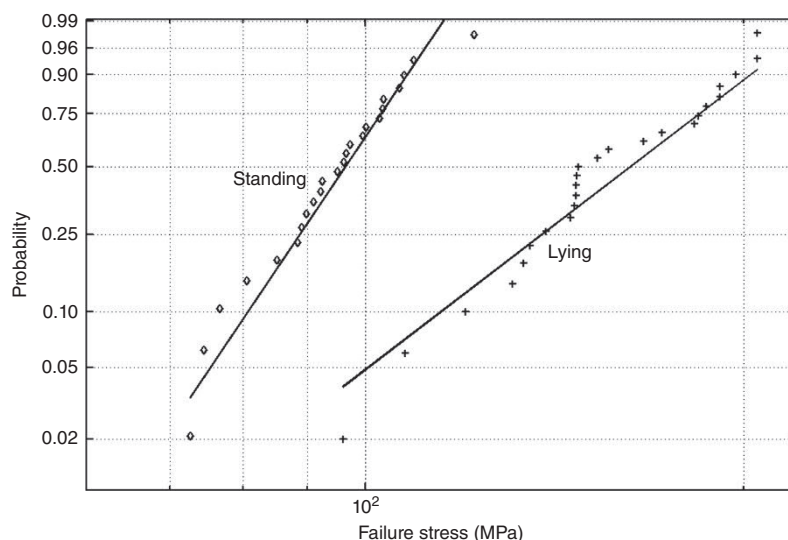


Figure 8 Weibull plot (see Chapter 3.11) for glass panels tested either standing (in-plane loading) or lying (out-of-plane loading) [8, 9].

codes take into account the uncertainty in individual glass pieces through partial safety factors and a number of other parameters, as discussed in Section 4.2. The statistics regarding, for instance, the appropriate frequency distribution behind these factors, however, are still very much debated [8, 11]. So is, therefore, the truly obtained level of reliability.

- **Static scheme:** because of the susceptibility of glass to peak stresses, the distribution of these stresses should be predictable. This condition generally means avoiding unnecessary constraints and statically indeterminate structures. If this cannot be avoided, the actual resulting stresses should be checked thoroughly.
- **Material:** glass-only structures are rare. Glass is usually combined with steel, although glass-timber structures also exist.
- **Sizing:** practically all glass used in buildings is soda-lime silicate produced through the float process, often simply referred to as float glass (Chapter 1.4). Thus, the material is only available as flat sheets with typically a maximum size of 6×3.21 m, although sheets with lengths of up to 18 m have become available. For schematic design, choices have to be made on how the structure will be segmented because it is actually impossible to weld or cast soda-lime silicate glass, contrary to other materials such as steel or concrete. Also note that a limited number of thicknesses are available for glass sheets. The standard values are 3–4–5–6–8–10–12–15–19–25 mm, the last three being increasingly expensive. Theoretically, it is possible to laminate a large number of glass layers together, but only double laminate is a standard product and accordingly priced.
- **Connections:** the type of connections needs to be selected on the basis of the size of the glass element

and the structural system. Options are further discussed in Section 5.

- **Possibilities for replacement:** glass can be damaged easily without any established repair agents such as mortars. As the damages are often also very visible, the very practical possibility to replace an element should not be overlooked in structural glass design. The importance of this constraint increases with the size of an element and its role in the structure. Besides, new pieces of special glass elements may not be available after a project is finished, or they may be very expensive or take a long time to be produced again.

3 Float-Glass Processing for Structural Applications

In structural glass engineering, two methods of glass processing are of vital importance: laminating and strengthening.

3.1 Laminating

Laminating is the bonding of two or more sheets of glass together by means of polymer interlayers (Chapter 9.2). Laminated glass has the significant advantage that breakage of one glass layer does not necessarily result in failure of the whole panel, as the other layer(s) may maintain the functionality. It is therefore the primary method to create redundancy and safety in structural glass.

By far the most common laminate material is polyvinyl-butyl (PVB) foil. This product was invented in 1903 and found an application in the windshields of cars in the 1930s. Commonly, one produces PVB-laminated glass

by layering the glass and PVB in an autoclave where, under increased pressure and temperature, the PVB melts and adheres to the glass. Vacuum bags are also used sometimes, particularly with complex shapes or individual (prototype) specimens. Other interlayer materials include ethylene vinyl acetate (EVA), which is used most in solar panels, modified PVBs (acoustic), and thermoplastic polyurethanes (TPU).

The so-called ionomer laminate foils (under the trade name of SentryGlas®) have been applied approximately since the beginning of the twenty-first century [12]. They have a much higher strength, stiffness, and tear resistance than regular PVB. Originally, this interlayer was developed to create glazing resistant to airborne debris in hurricanes. But it has also significant advantages from a structural engineering point of view. Within a larger range of temperatures, it allows the section to work more as a monolith, rather than as a layered structure. This property greatly increases the stiffness of a panel and results in a significant residual strength even if all glass sheets in a laminate are broken, something that one cannot achieve with softer foils such as traditional PVB. Other stiff interlayer foils are also being applied nowadays, such as the Saflex DG Structural Interlayer, a PVB with an adapted formulation.

Apart from foil interlayers, resin-based interlayers can be applied. These are poured in a thin cavity between glass sheets in a liquid state and then cured. During curing, the interlayer adheres to the glass. Because of their

low tear resistance, resin-based interlayers are seldom used nowadays.

3.2 Thermal Prestressing

Whereas laminating is primarily done to increase safety, strengthening is applied to increase long- and short-term resistance to tensile (peak) stresses (Chapter 3.12). Usually, strengthening is achieved by thermal prestressing, which involves heating evenly the glass sheet to a temperature of around 720 °C, and quenching it by blowing cold air over the surfaces (Figure 9). This causes the outer surface of the glass to solidify without shrinking. The inner core, which cools at a slower rate, shrinks during solidification, thus creating compression in the outer surface, and tension in the core. With thermal prestressing, the stress profile is parabolical through the thickness (Figure 10).

As glass fracture always starts from peak tensile stresses around defects in the glass surface area, putting the surface into compression results in a higher load-bearing capacity of the glass sheet: the surface compression thus has to be overcome before tensile peak stresses can develop. Another major advantage of the surface compression layer is that it provides significant protection from stress corrosion, as the surface only comes into tension under extreme loading conditions. In thermal prestressing, a distinction is made between heat strengthened and thermally tempered (or toughened) glass.

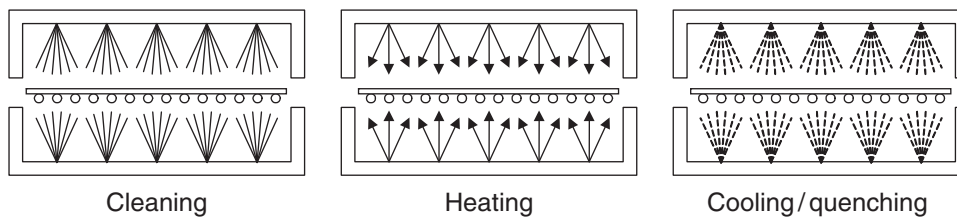
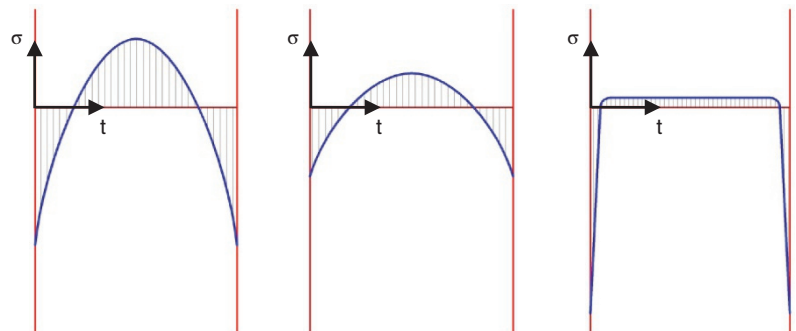


Figure 9 Schematic representation of the thermal tempering process [13].

Figure 10 Through the thickness stress profiles of strengthened glass, from left to right: fully tempered (or toughened), heat strengthened, and chemically strengthened [6].



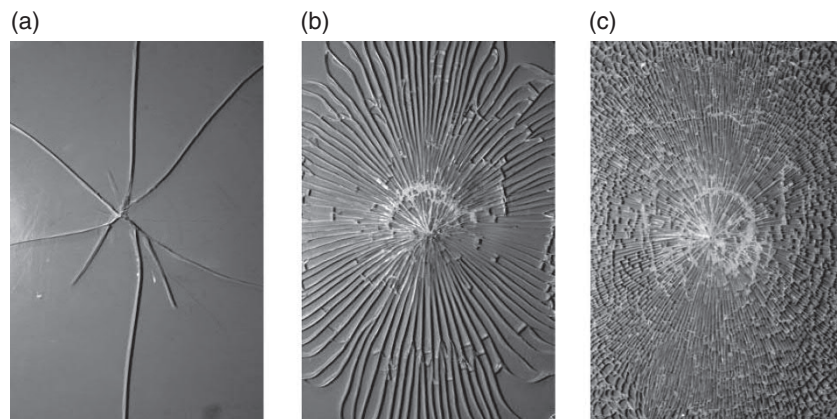


Figure 11 Fracture pattern of (a) annealed, (b) heat-strengthened, and (c) fully tempered glass [2].

The load-bearing capacity of thermally prestressed glass is usually defined as the sum of the surface compression stress introduced by the thermal process and the short-term bending tensile strength of annealed float glass ($\sigma_t = 45$ MPa for a 95% fractile; the surface compression is considered 0 MPa, although in reality this is usually several MPa). European codes such as NEN 2608:2014 [14] require $\sigma_{t,95\%} \geq 120$ MPa for tempered glass and $\sigma_{t,95\%} \geq 70$ MPa, which implies minimum surface compressions of 75 and 25 MPa, respectively. Research [8] has shown that this simple summation approach is not completely valid to describe the load-bearing capacity of thermally prestressed glass, but that it remains a sufficiently accurate approximation in structural glass engineering practice.

Besides the surface-compression level, the major difference between tempered and strengthened glass is the fracture pattern (Chapter 3.12). The former breaks into very small dice-like fragments, whereas the latter has a fracture pattern more similar to that of annealed glass, i.e. yielding relatively large shards (Figure 11). This is considered an advantage in structural applications of laminated glass panels, as it allows a degree of residual strength and stiffness in a heat-strengthened laminate after breakage. In contrast, a thermally tempered laminate will act as a wet blanket after breakage of all layers. This may result in collapse of the panel, for instance, by tearing and/or slipping from its (point) supports. The combination of increased strength, stress corrosion resistance, and favorable fracture pattern has thus led heat-strengthened glass to become the preferred material in structural glass engineering.

Although major prestresses are created in this way in the glass surface, it is important to realize that they are not evenly distributed throughout the whole sheet. As a result of boundary effects, the cooling differential between the inner sheet and the outside is smaller at the corners, along the edges and around holes. The level

of prestress that can be achieved is therefore lower in these areas. Structural glass codes provide instructions on the size of these areas (generally about 1–1.5 times the thickness) and the prestress reduction that should be taken into account, which can be up to 100% at the corners according to codes such as the NEN 2608:2014 [14]. If the highest stresses occur in these areas, the application of thermally prestressed glass may not be as advantageous as one would think from the general level of prestress that can be obtained.

As described in Chapter 3.12, a problem found for thermal prestressing, particularly tempering, is the failure caused by the presence of nickel-sulfide inclusions in the glass, which can take up to 10 years to manifest itself on north-oriented façades.

3.3 Coating

Often, coatings are applied to one or both surfaces of a glass sheet (Chapters 6.7 and 8.2). Metallic coatings, for instance, reflect sunlight selectively with regard to wavelength, i.e. they can be adjusted to reflect certain parts of the daylight spectrum (Chapter 6.8). As the 390–750 nm visible spectrum represents a small part of solar electromagnetic radiation, significant reductions of transmitted solar energy (g -value) can be obtained without grossly compromising the transparency. For instance, neutral solar reflective glazing can transmit around 70% of the visible light (untreated glass: around 80–85%), with a g -value of only 40% (in commercial products, these numbers are often added to the product name, in this case as 70/40). Therefore, the application of metallic coatings to façade and roof glazing has now become commonplace.

Organic coatings are also applied increasingly. Often dubbed “self-cleaning,” they make it difficult for particles to adhere to the glass surface, resulting in decreased need for cleaning, although they do depend on rain to let the panel actually be cleaned.

Metallic and organic coatings are too thin to have any structural function. There has been research into the possible effects of stress corrosion reduction and protection from surface damage [10, 15], but this direction has not been pursued extensively and has not led to generally accepted or understood results.

3.4 Mechanical Processing

In spite of the troublesome brittleness of glass, several ways of mechanical processing have been developed. Cutting is the most common method to obtain a glass sheet of the required size. This involves scoring the glass with a cutting wheel on one side and subsequently breaking it. Straight cutting can be done either manually or with a machine if not on site, but training is required to make clean cuts through glasses thicker than 12 mm for which obtaining a clean break is more difficult. Some machines are capable of cutting two-layer laminates by scratching each of the glass sheets on the opposite surface. Cutting in curves is also possible. Other methods are machine-disc sawing, water-jet, and laser-jet cutting, but they are more time consuming. These techniques can be applied to obtain glass panels of any shape.

After cutting a panel to size, the edges are often beveled, ground, and sometimes polished to obtain smooth edges, safe to touch, and with smaller edge defects. This is particularly important when the edges are in sight (and can be touched), or when significant edge stresses are expected, for instance, because of differential thermal expansion loads.

Techniques have been developed to drill holes in glass sheets with purpose-made diamond-covered drills. These are used for point-fixed glazing. If the glass is to be prestressed, the holes should be drilled before the thermal treatment. This requirement may cause alignment problems if the panel is then also to be laminated. Drilling can only be done under controlled conditions in a shop, otherwise it is very likely that it will either cause immediate breakage or result in large surface flaws that may cause premature failure later. Unless for diameters of at least 40 mm, it is not possible to polish the inside of a drilled hole. A reduced strength should therefore be accounted for when the edge of a drilled hole is loaded.

4 Design and Detailing

4.1 Safety Approaches

Owing to the failure behavior of the material, the safety of a glass structure requires specific attention [6]. The basic assumption should be that all the glass in the structure can break. The extent to which this precaution is taken

into account depends on the risk profile of the application (i.e. a broken window pane is less of a problem than a broken glass floor element). In their most elaborate form, quantified requirements are set for:

- The resistance, particularly against specific actions such as drop and sway impact with hard and/or soft bodies.
- Residual resistance for a specified period of time, making distinction between residual resistance at increasing levels of damage (one, more, or all glass layers broken).

Modern structural glass codes apply this approach.

To determine the risk profile, qualitative or quantitative scenario approaches can be applied in which the possible causes of damage are systematically reviewed. The extent of such an analysis depends on the particularity of the application. Typical scenarios can include collision with road vehicles, cleaning machines, vandalism, bomb-blasts, etc. A scenario approach should include consideration of the possible loading after the incident and the time required to take protective measures and to make replacements.

There are basically two strategies to avoid detrimental effects of glass failure, which are often combined: reducing (i) its probability and (ii) its consequences.

An important way to reduce the probability of failure is to maintain high-quality standards throughout the design and construction process, including thorough design review, specialist training of handlers and construction workers, production quality control (e.g. heat-soaking for thermally treated glass, which speeds up the α - β -transition of nickel sulfide inclusions), and even well-specified transport and storage conditions. Also, it is important to avoid excessive time and financial pressure, as glass failure is more often than not caused by errors in the design, production, handling, transport, or construction. As damage is often caused by incidental impact, applying protective measures such as edge covering or physical anti-collision elements can also significantly reduce failure probability.

Because reducing the probability of breakage is not enough to obtain an acceptable level of risk, measures also have to be taken to reduce the consequences of a failure. As it is impossible to improve sufficiently the material properties themselves, glass is usually laminated (see Section 3.2). This results in transparent composite elements with significantly higher resilience. Generally, as long as at least one glass layer remains unbroken, such an element will possess significant residual strength. Experimental research has shown that laminating provides an effective barrier to macroscale crack growth through structural elements. Depending on the layout, interlayer material, and level of prestress (i.e. tempered,

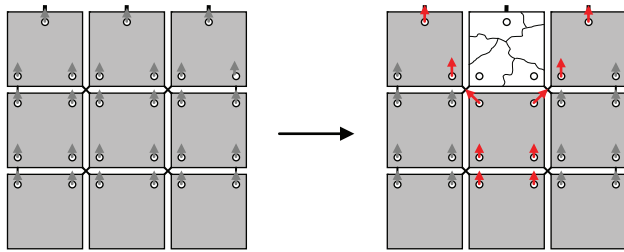


Figure 12 Principle of the alternative load-path design in the hanging glass façades of Cité des Sciences at La Villette in Paris: the panels are joined with cross-shaped connectors, allowing a redistribution of loads through adjacent panels in case one should break [6].

heat strengthened, or annealed), the element may still possess significant residual strength even if all glass layers are broken. If very high safety standards are required, steel profiles may be added to such a glass laminate to obtain very high residual strengths (see Section 6.5). If applied to glass beams, this often results in strain hardening behavior, and thus to failure behavior comparable to that of reinforced concrete [13].

In addition to reducing the consequences of failure of the structural *elements* themselves, it is possible to apply measures in the overall *layout of the structure*, in the form of alternative load paths. Such a scheme is shown in Figure 12 for a façade of glass panels hanging one from

another. The cross-shaped connection elements allow the loads of a panel beneath another one incidentally broken to be carried by the adjacent rows of panels. Another example (Figure 13) is that of a catenary reaction that will be activated perpendicular to the main load-bearing direction in case a glass beam would fail. Generally, the maximum load and stiffness of such an alternative load path is significantly lower than that of the primary load path.

4.2 Structural Analysis

At first sight, calculations of the structural behavior of glass are rather simple since a linear elastic response is assumed up to failure. Generally, a Young's modulus of 70 GPa is retained, although measurements have shown that actual Young's moduli may vary roughly between 65 and 75 GPa.

Nevertheless, some particularities should be considered:

- Because of the susceptibility to micro- and macrosized surface defects, the strength of individual glass sheets shows a large scatter. In structural analysis, one usually accounts for it by applying significant material partial safety factors (e.g. $\gamma_M = 1.8$ for analysis with wind loading, 2.0 for other loads according to NEN 2608:2014 [14]).

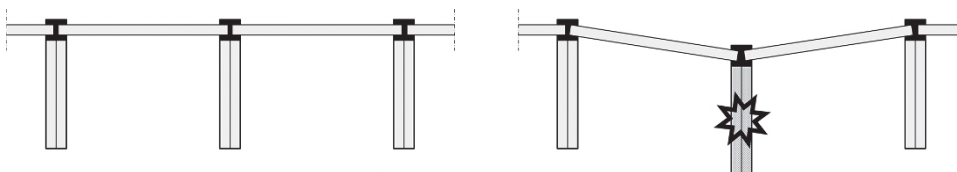


Figure 13 (a) Wolfson Building glass roof, Glasgow, UK, (b) schematic section of the glass roof, in undamaged condition, (c) schematic section after fracture of one of the glass beams. If, for whatever reason, one beam fails, loads can be redistributed to the adjacent beams through catenary action (perpendicular to the beam length axis) in the roof panels [6].

- The strength depends on the humidity and tensile stress history (which induces subcritical crack growth). In strength analysis, this variability is usually covered by a factor k_{mod} , which ranges approximately from 0.3 for permanent loads to 1.0 for (five seconds) wind loads. In structural calculations, different checks should be made for each governing action with different durations.
- The edges of a glass sheet possibly have larger surface defects than the front and back faces. The location where a stress acts should therefore be considered and, in most cases, specifically checked since failure can take place at a lower strength if the stress is applied to the edge compared to a face.
- In heat-treated glass, the strength results from differential cooling rates and, therefore, depends even more on location than in annealed glass. Along edges and bore-holes, the effect of heat treatment is reduced. At the corners it should even be considered nonexistent. Different checks may be required, depending on the stress distribution.

For glass, another difficulty is that one cannot rely on any a priori form of stress redistribution. Therefore, unless the structural design presents a clear-cut analytical solution, finite element modeling is often applied to locate and quantify local peak stresses. Geometrically nonlinear analysis is usually called for, as elements tend to be slender (great length and width compared to thickness), resulting in nonlinear deflection behavior in out-of-plane loading (e.g. façade panels) and stability problems in in-plane loading (e.g. beams).

Because glass plates are often assembled into laminates for safety reasons, their structural properties are also determined by the mechanical properties of the interlayer material. As these are always polymers, their behavior depends on a number of parameters of which load duration and temperature are the most important. Together with the material composition, they determine the effective stiffness and, thus, the extent of coupled action of the glass sheets in a laminate. Specialist software exists in which the most relevant interlayer properties, load durations, and temperatures have been incorporated.

5 Connections

5.1 General Considerations

Over the years, several kinds of connections for (structural) glass members have been developed. In the present chapter, a distinction is made between mechanical and adhesive connections. The former typically involve metal parts such as steel plates and bolts that either clamp around the glass or penetrate through it, whereas

adhesive connections generally involve (metal) parts bonded to the glass surface. Mechanical connections are most traditional and most commonly applied, the more so because adhesive connections – apart from structural sealant glazing (see Section 5.3.1) – currently suffer from uncertainties in durability and long-term behavior.

In view of the variety of designs, it is not possible here to cover them all in detail. Rather, we will focus on typical examples of both kinds. However, a few key points should be mentioned first.

Connection forces can be transferred at the surface, at the edge, or at a bore-hole edge of a glass member. At the surface, the forces are commonly transferred via contact pressure, friction, or shear interaction (e.g. adhesive bond), whereas contact pressure is involved at the edge (e.g. setting blocks) or borehole edge (e.g. bolted connections). Besides, all machining (e.g. cutting, grinding, polishing, drilling, or laminating) should generally be done before the glass members are assembled because, as already stated, the material cannot easily be tailored on-site. This complication affects the connection design and implies that careful consideration of tolerances should be taken. In addition, it is essential to avoid direct contact between glass and “hard” materials such as steel, concrete, stone, etc., which may cause high local stress concentrations and cause fracture of the glass. To avoid direct contact, “soft” intermediary materials such as neoprene, pure aluminum, nylon, or EPDM are often used. Finally, hinged connections are generally preferred, as they limit force concentration compared to rotationally rigid connections.

5.2 Mechanical Connections

5.2.1 Mechanical Point-Fittings for Façade Glazing

Mechanical point-fittings are often applied to connect glass panels to one another and/or to the supporting substructure (Figure 14). These connections are generally applied for glazing in façades. A schematic overview of typical point-fittings is provided in Figure 15.

Clamped point-fittings, as shown in Figure 15a, basically consist of small (metal) plates that clamp the glass panel back to the supporting substructure. Often EPDM gaskets are applied to avoid direct contact between the metal clamping plates and the glass. The clamped point-fittings are typically positioned at the perimeter of the glass panel and carry the out-of-plane loads that act on it. The in-plane loads are normally carried separately by settings blocks at the edge of the glass.

Drilled and bolted point-fittings, such as shown in Figure 15b–d, are made by means of metal bolts and holes in the glass. These holes can either be made by means of cylindrical (Figure 15b), countersunk (Figure 15c), or

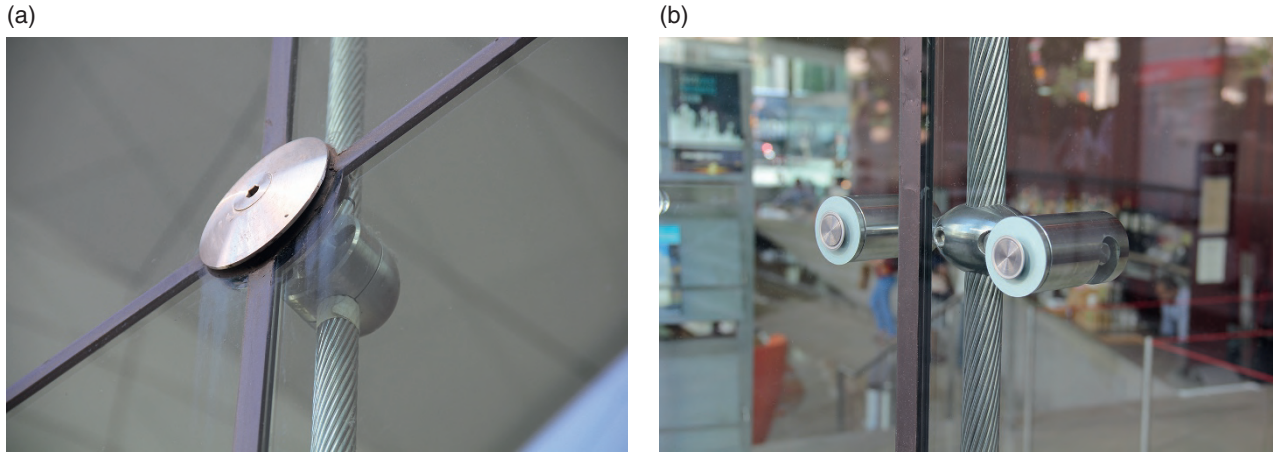


Figure 14 Examples of point-fittings in glass façade. (a) Clamped point-fitting, (b) drilled point-fitting. Source: Photos C. Louter.

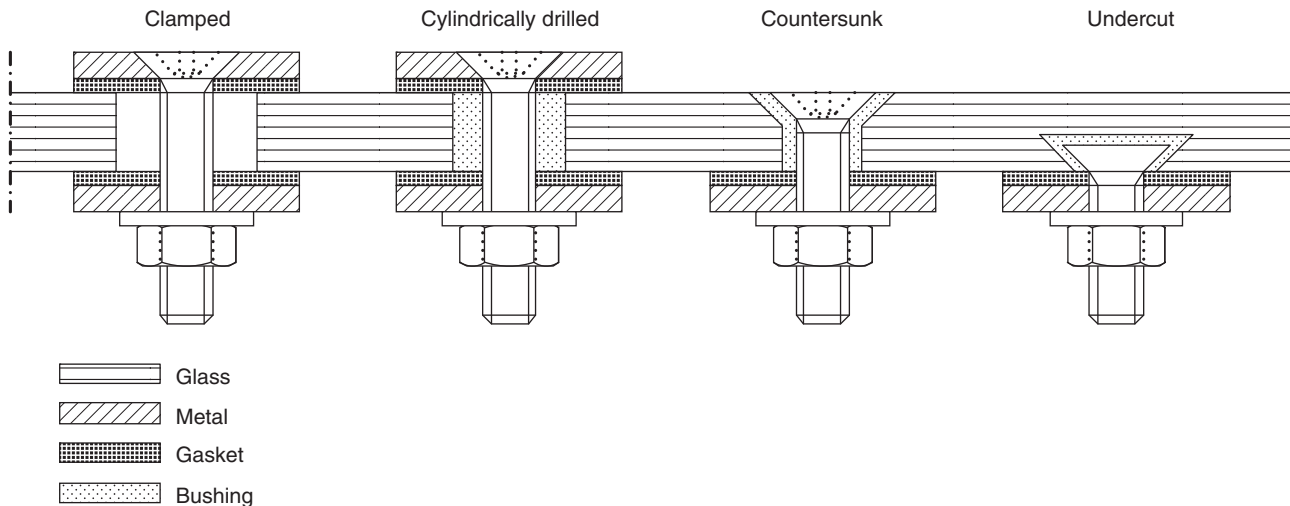


Figure 15 Schematic overview of point fittings for glazing. (a) Clamped, (b) cylindrically drilled, (c) countersunk, and (d) undercut.

undercut drillings (Figure 15d), preferably followed by grinding and polishing of their perimeters. The bolt is positioned into the drilled hole and fixes the glass panel to the substructure. These point-fittings are suited to carry out-of-plane loads, but can carry only limited in-plane loads. To avoid direct contact between the bolt and the glass, often bushings (e.g. nylon, pure aluminum) or mortars are applied. Furthermore, since these point-fittings often impose a relatively high local stress at the perimeter of the hole in the glass, the use of heat-treated glass is commonly required.

Another important aspect is that free rotation of the point-fittings should be provided to prevent high stress from concentrating at the point-fitting when the glass panel is bending because of out-of-plane loads. This

can be achieved by means of articulated bolts. Furthermore, to allow (thermal) movement differences between the glass panel and the supporting substructure, oversized or slotted holes should be provided at the bolt-connection to the substructure (Figure 16). These oversized and slotted connections allow for in-plane movement of the panel.

5.2.2 Linearly Supported Façade Glazing

Another example of mechanical connections can be found in façade panels that are clamped in a supporting frame at the perimeter of the glass. The out-of-plane loads on such panels are transferred to the (metal) support frame in a linear manner through contact pressure at the glass surface. To avoid direct contact between

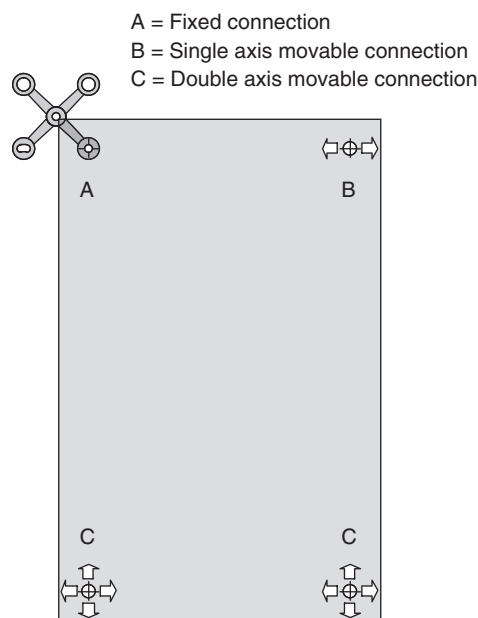


Figure 16 Schematic overview of required allowable in-plane movements of point-fixed façade panel.

the glass surface and the frame, a gasket (e.g. EPDM) is commonly applied. The in-plane loads, however, are not transferred linearly, but by contact pressure through settings blocks at the (bottom) edge of the glass panel.

5.2.3 Through-Bolt Point Connections for High-Force Transfer

The through-bolt connection type [2] is meant for transferring high in-plane forces (Figure 17). It is typically found in structural glass beams and fins, either to connect to the surrounding structure or to join beam segments. The connection consists of a bolt/pin that is inserted in

a hole in the glass and transfers the force between the glass and two outside metal plates. The bolt itself is mostly loaded in shear whereas the forces are transferred to the steel and the glass through contact pressure at the hole perimeter. To avoid direct contact between the bolt and the glass, a bushing is provided around the bolt. For laminated glass, for which the holes in the individual sheets are drilled prior to the lamination process, often an injection mortar is applied to even out any alignment differences between the hole edges. But the main drawback of this connection type is that it requires drilling of the glass, which causes local damage and consequent glass strength reduction at the perimeter of the bore hole. Combined with the localized force transfer, which causes high peak stresses at the (weakened) perimeter of the bore hole, bolted connections in glass are relatively inefficient.

5.2.4 Friction Connections

Friction is involved in the last type of mechanical connection to be discussed here, which also makes use of a bolt that is inserted in a hole in the glass. However, the purpose of the bolt is to clamp tightly two outer metal plates to the glass (Figure 18). The bolt is torqued to a level such that sufficient surface friction is generated to transfer in-plane forces. The hole in the glass is oversized and the bolt does not transfer forces to its edge. Between the steel clamping plates and the glass, friction-enhancing materials could be provided. For laminated glass, a local rigid insert should be provided between the individual glass sheets to avoid creep of the polymer interlayer that would cause loss of prestress in the bolt or fracture of the glass. Friction connections are typically applied for transferring high in-plane forces and can be found in segmented glass beams (Figure 3) or segmented glass façade fins.

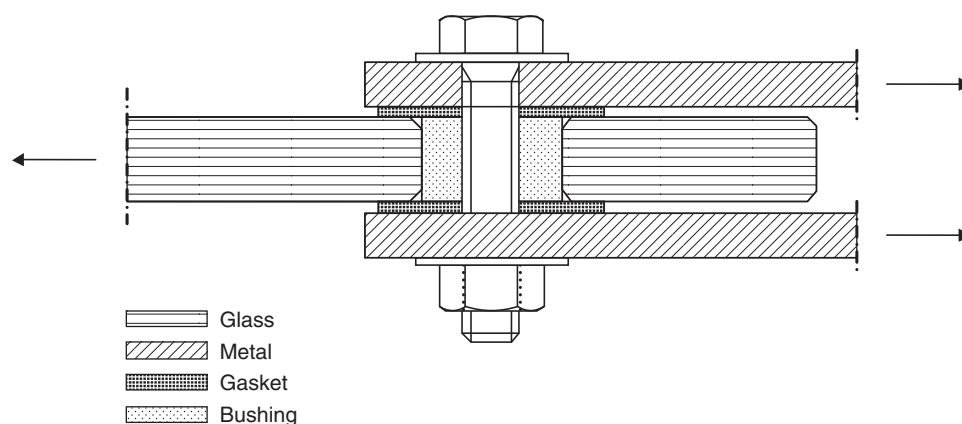


Figure 17 Through-bolt connection. For laminated glass alternative, see [2]. Source: Drawing based on [2].

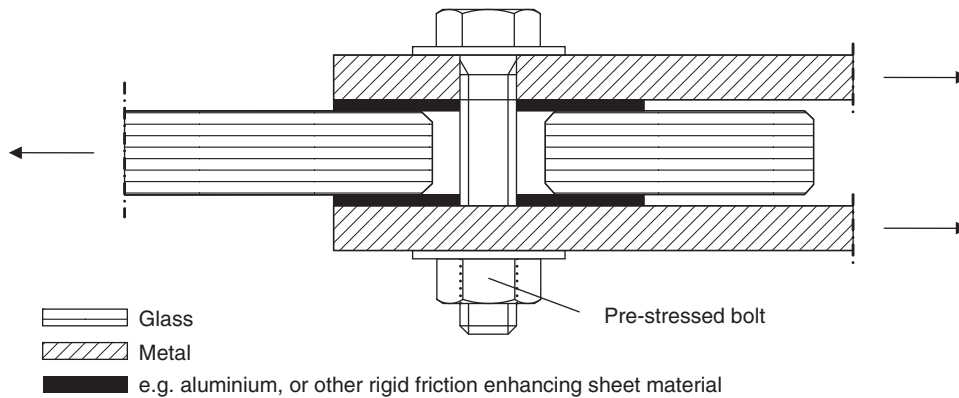


Figure 18 Friction grip connection. For laminated glass alternative, see [2]. Source: Drawing based on [2].

5.3 Adhesive Connections

5.3.1 Overview

Adhesive connections can appear in different geometries, such as linear, point, and large area. They are attracting significant interest in structural glass engineering as they have several potential advantages over mechanical and, in particular, over bolted connections [16]. The main benefit is that no glass drilling is involved – thereby avoiding local weakening of the glass – and that the forces are spread over a relatively large bond area, which implies that the associated stress is reduced. Among structural adhesives such as epoxy, acrylic, polyurethane, and silicone, the last is rather flexible and commonly used for Structural Sealant Glazing (SSG) systems whereas the others – especially the epoxy and acrylic adhesives – can provide very strong and rigid connections. In addition, adhesives such as transparent structural silicone adhesive foil or the aforementioned ionomer interlayer are gaining interest for bonding metal components to glass through an autoclave lamination process [17]. An overview and broad screening of adhesives for glass-metal bonding is provided in [18].

With the exception of SSG systems, however, uncertainties in quality control, durability, and long-term performance hinder the wide application of adhesives in glass structures. These uncertainties often cause restrictions by authorities who generally require additional mechanical connections. This especially applies to permanent loads, such as dead loads of panels.

Furthermore, adhesive connections raise some specific questions. Because adhesives are viscoelastic substances, their structural response depends on load duration and temperature. Long-term loading causes creep/relaxation, whereas increasing the temperature generally leads to a reduction in shear modulus. Furthermore, adhesive connections are preferably loaded in shear while peel forces

should be kept to a minimum. Especially for linear adhesive connections, the stress induced by thermal expansion differences between the adherents should be carefully taken into account. Additionally, the design of adhesive connections cannot rely on a calculation of the average stress in the adhesive bond (Force/Area) because local stress concentrations within it govern the strength of the connection. Finally, from a practical point of view, adhesive connections are generally and preferably not executed on-site, but pre-executed in a protected environment (factory) to keep the bond surface clean and to perform the specific surface pretreatments that are generally required to obtain proper adhesion.

5.3.2 Linear Adhesive Connections in SSG Systems

Linear adhesive connections are typically applied in SSG systems for creating glass curtain wall façades. In an SSG system, the glass panels are bonded in the factory by means of a structural silicone to a metal subframe. After curing of the adhesive, the metal frame and the glass panel as a whole are transported to the building site, hoisted in place, and mechanically anchored to the building structure. The linear structural silicone connection is intended to carry the out-of-plane loads on the glass panel, whereas the dead load of the glass panel is often carried by mechanical supports (at the lower glass edge).

Structural silicones basically exist as one- or two-component products, which cure with air moisture or by a chemical reaction between a base component and a catalyst, respectively. Structural silicone adhesives typically have a rather low Young's modulus of elasticity ($E = 1\text{--}2\text{ MPa}$ [19]) and exhibit rather low tensile and shear strengths (a typical design stress is around 140 kPa, although ultimate tensile stresses can reach between 1 and 2 MPa [20]). They are typically applied in thicknesses of 6–20 mm and with a thickness-to-width ratio in the

1 : 1 to 1 : 4 range [2]. Thanks to their large thickness and low E -modulus, silicone joints are rather flexible, which is beneficial for compensating for thermal expansion differences between the glass and the metal subframe.

Even under clean conditions, primers are often required to promote adhesion whereas surface coatings on the adherents are preferably avoided as they may reduce it. Furthermore, for structural silicones, it is important to check their chemical compatibility with the materials with which they are in contact, such as EPDM gaskets, interlayers in laminated glass, and settings blocks, as these polymeric materials may cause their discoloration and degradation.

In Europe, silicone adhesives applied in structural applications must be approved by means of a European Technical Assessment (ETA). For this purpose, the European Organization for Technical Assessment (EOTA) provides a European Technical Assessment Guideline (ETAG), namely ETAG 002 for Structural Sealant Glazing Kits, which consists of three parts [21]. In these ETAG documents, requirements and testing procedures – such as tensile, shear, durability, and compatibility tests – are provided to which the structural silicone should comply in order to receive CE-marking.

5.3.3 Adhesive Point Connections

A promising alternative for hole drilling and mechanical point-fittings in façade glazing is to bond adhesively a metal puck or connector to the surface of the glass and connect it mechanically to the substructure. Epoxies and acrylates are often used for these kinds of point connections. These adhesives are typically applied in thicknesses in the range of 0.1–3 mm, which guarantees a stiff connection between the glass and the metal connector. Also silicone and ionomer foil adhesives are gaining interest for creating adhesively bonded point-fixings [17, 18, 22, 23].

Although several (research) projects demonstrate the potential of adhesively bonded point connections, their application in practice is currently limited by the aforementioned uncertainties in durability and long-term behavior of the adhesive. Research nonetheless continues to push forward the field of adhesive point connections in structural glass engineering.

5.3.4 Large-Area Adhesive Bonds

Occasionally, large-area adhesive bonds are applied for connecting glass beams to glass columns in portals (Figure 19), which is typically done by means of multilayer laminated glass components [1]. At the intersection between the glass beam and column, the outer glass layers of the beam are stopped short of the end of the beam. For the glass column, the opposite is done, so that a “spliced” connection is made in which the glass beam is inserted into the glass column, as

indicated in Figure 19a. The inverse, as indicated in Figure 19b, is also possible. Alternatively, glass patch plates can be applied, as indicated in Figure 19c, to overlap and connect the inner layer of both the beam and the column. In both cases, transparent setting blocks are positioned between the glass edges of the column and the beam to carry the vertical forces and to prevent direct glass-to-glass contact. At the intersection/overlap of the beam and column, the gap between the glass layers is sealed along the edges and filled with a transparent resin or acrylate adhesive. This chemical is then commonly exposed to a UV-light source which triggers its polymerization. As such, a fully transparent joint is created between the glass beam and glass column.

A second application of large-area bonds can be found in splice-laminated large-span glass beams, fins, or façade panels. In these beam/fin/panel configurations, one creates large-span glass components by laminating several shorter glass segments in overlap (Figure 20) [24]. The individual segments are joined by means of polymer interlayer sheets and are laminated through an autoclave lamination cycle. In the finished product, all interaction between the glass segments is provided through the large-area interlayer bond. This specific technique enables the fabrication of oversized glass components making use of regularly sized glass panels, which may be attractive from a practical and/or economical point of view.

6 Perspectives

Notwithstanding what has already been achieved in structural and architectural applications of glass, a diversity of further exciting developments is currently being explored in research, or already making its way into construction practice [25]. These innovations are likely to enhance the structural and architectural possibilities of glass even further in the (near) future, and are (briefly) discussed in the following subsections.

6.1 Glass Sheet Size

The standard maximum size of a glass sheet for a long time has been 6.00×3.21 m. The width was limited by float-line dimensions, the length by handling and shipping standards and constraints. The glass processing facilities have also been adjusted to this maximum size, or often smaller. This situation changed about halfway the first decade of the twenty-first century when float glass of up to 18 m length became available (see [25] for example applications). Autoclaves and prestressing ovens were also updated to be able to laminate and

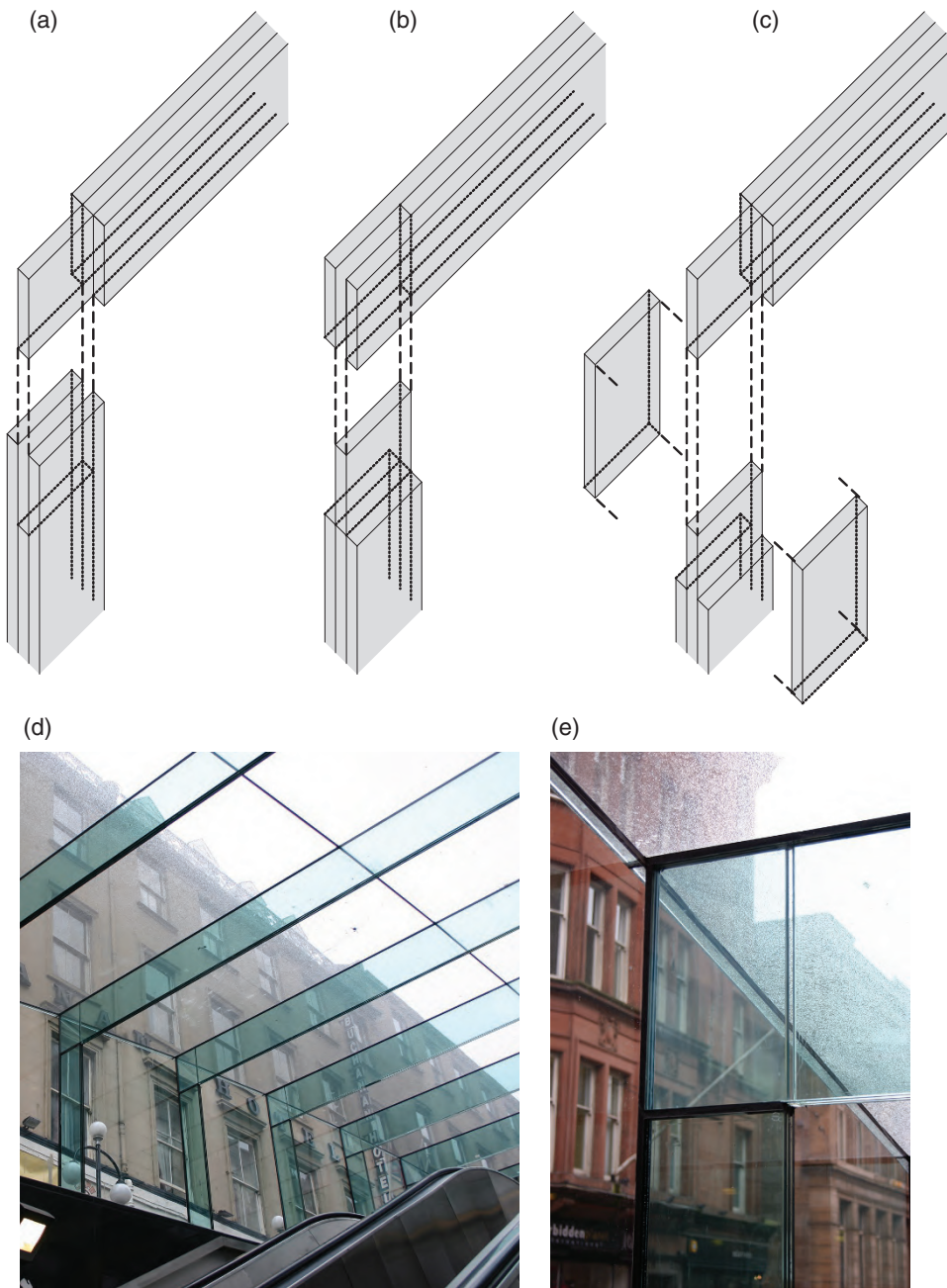


Figure 19 Spliced beam-column connections. (a–c) Principles, based on [1]; (d and e) applications in the Buchanan Street Underground metro station entrance, Glasgow; Dewhurst Macfarlane & Partners. Source: Photo C. Louter.

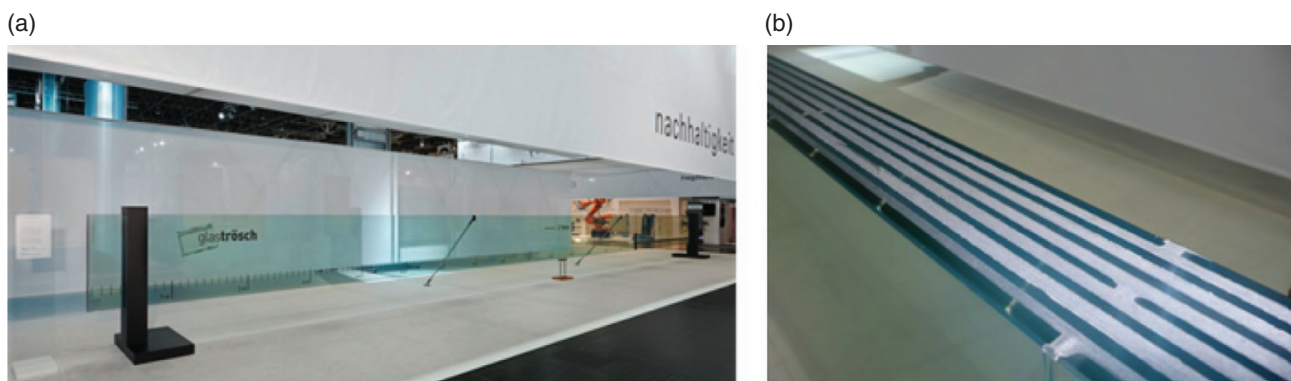


Figure 20 Splice-laminated large-span (21 m) glass beam, (a) overall view and (b) close-up, demonstrated by Glas Trösch/Euroglas at GlasTec 2010 [24].

thermally prestress those sizes. Since then, the number of manufacturers and processors able to handle 6+ m sizes has grown steadily, as has the number of projects in which such sheets have been applied [49]. Currently, glass sheet sizes between 6 and 12 m length are no longer extremely rare although lengths of more than approximately 12 m are still unique. This may be due not only to the cost of such elements in the initial construction, but also to the financial in-service risk. Replacing such an element in case of (accidental) damage is expensive, time consuming, and intrusive to the particular structure. Additional care and consideration in design and construction is therefore required.

6.2 Cold Bending

Developments in architecture since the end of the twentieth century have hugely increased the popularity of non-orthogonal shapes. Curved glass components for building applications are traditionally produced by means of a hot-bending process. However, this technique has some disadvantages, such as high costs for molding, high energy consumption, inefficiency in transport of the curved components, and risk of optical distortions. Therefore, alternative cold bending techniques are currently gaining significant interest for building applications [26].

With these techniques, one “simply” elastically curves, warps, or twists flat-glass panels at ambient temperature to the desired shape and subsequently fixes them into position. This solution is economical as it does not require expensive molding or high energy consumption for heating the glass. Furthermore, optical distortions are minimized and the resulting reflections are smooth. The degree of curvature is more restricted than for hot bent glass, however, because of the applied permanent

bending stress on the glass. Therefore, cold bent glass generally requires the use of fully tempered glass, which has enhanced strength and does not suffer from stress corrosion phenomena as long as the compressive prestress is not overcome. Additionally, the thinnest possible glass panel is generally adopted to minimize the bending stress. Minimal curvatures of $1500t$, with t = glass thickness are generally accepted, but in cases bending radii as small as 3.0 m can be applied.

Cold bending by assembly is most common. In this respect, an often applied strategy is to curve flat-glass panels over a pre-curved (linear) subframe and to clamp them into position. This can also be done using special devices that pre-curve the glass panel airborne before mounting it to the (curved) substructure [27]. Another strategy concerns mounting flat-glass panels by means of point-fixings and subsequently forcing one or multiple point-fixings out-of-plane to create the curved glass surface. Though less commonly applied, an alternative *cold bending by assembly* strategy is to assemble flat-glass panels to a linear subframe and to curve/warp the assembly as a whole.

Yet another method is the *cold bending lamination process*. Several glass layers are bent to the desired curvature, stacked with intermediate interlayers and subsequently laminated by means of an autoclave lamination procedure during which the interlayers adhesively bond the glass layers. Thanks to their shear stiffness, the interlayers are able to keep the glass layers in the curved position. However, specific points of attention are the initial springback upon release of the laminate and the creep/relaxation response of the interlayer over time.

Several projects involving cold bending of glass have been completed over the recent past years (Figure 21). Furthermore, an increasing number of academic studies

Figure 21 Curved glass envelope realized by means of cold bent glass, Strasbourg railway station, France. Source: Photo M. Denancé.



are advancing on this topic [28–30], focusing on issues such as the springback relaxation effects of glass panels produced by a cold bending lamination process and the buckling behavior of cold bent glass panels.

6.3 Custom Cast Glass

Casted glass blocks for semitransparent applications (mostly partitioning walls) have been common for considerable time and are not of particular architectural quality. However, occasionally, projects arise for which high-quality custom cast glass elements are used to create striking visual results. A recent example is the Crystal Houses project in Amsterdam, the Netherlands [31, 32], which features a traditional Dutch brickwork and timber façade having been remade completely in glass, with cast bricks and window frames (Figure 22). Previous projects included the March 11 memorial in Madrid, Spain, and the Ice Falls entrance to the Hearst Tower in New York, USA. Such projects, however, seem to remain one-offs, rather than become main stream.

6.4 Adhesive Point Connections

Adhesive bonds, discussed in Section 5.3, particularly high-transparent point connections, are likely to be pushed by architects because of their high aesthetical quality. It may be expected that such connections will become the standard in due time. Extensive testing on reliability, failure behavior, and durability, as well as

further showcase projects are probably required to gain acceptance from authorities.

6.5 Hybrid Glass Components

A steadily increasing trend exists in the development of hybrid glass components that can provide several advantages over common structural glass components [33, 34]. These components consist of glass – typically as the main load-carrying material – and an additive material (e.g. metal, timber, carbon fiber reinforced polymer, glass fiber reinforced polymer) which are joined by means of an adhesive bond or a bolted connection. The hybrid components are intended to outperform common structural glass components by providing enhanced pre-fracture performance, postfracture performance, or a combination of both.

In terms of enhanced *pre-fracture* performance, a hybrid glass component can provide increased in-plane or out-of-plane bending stiffness. For instance, a hybrid glass sandwich component that consists of two outer glass panels and an adhesively bonded inner spacer can show superior out-of-plane bending stiffness compared to a regular glass panel. Furthermore, hybrid glass beams consisting of a glass web and additional flanges made of steel or timber show enhanced (out-of-plane) lateral torsional buckling stability [35] (Figure 23).

In terms of enhanced *postfracture* performance, hybrid glass components can provide significant postfracture strength and redundancy. One can achieve this



Figure 22 Cast glass block facade, Crystal Houses, Amsterdam, (a) overview, (b) close-up; MVRDV, ABT, TU Delft. Source: Photo F. Oikonomopoulou [31, 32].

postfracture strength by bonding additional reinforcement at the tensile side of the glass component. In case of glass fracture, the reinforcement will bridge the crack(s) in the glass and will carry the tensile force. This



Figure 23 Glass beam with adhesively bonded steel flanges [33].

postfracture load-carrying mechanism provides significant redundancy to the structural glass components and enables them, if cracked, to carry significant load. The validity of this concept has been demonstrated both for structural glass beams with reinforcement bonded at the tensile edge, e.g. [13] (Figure 24), and for glass panels with reinforcement mesh laminated between the glass layers [36] (Figure 25).

Finally, in terms of enhanced *pre- and postfracture* performances, it is worth to also mention post-tensioned glass beams [34]. In these beams, a compressive prestress is imposed by means of (steel) post-tensioning tendons which are either mechanically anchored at the glass beam ends or adhesively bonded along the beam length [37]. This compressive prestress enhances the tensile (bending) strength of the glass and thus increases the initial fracture strength of the glass beam. Furthermore, after glass

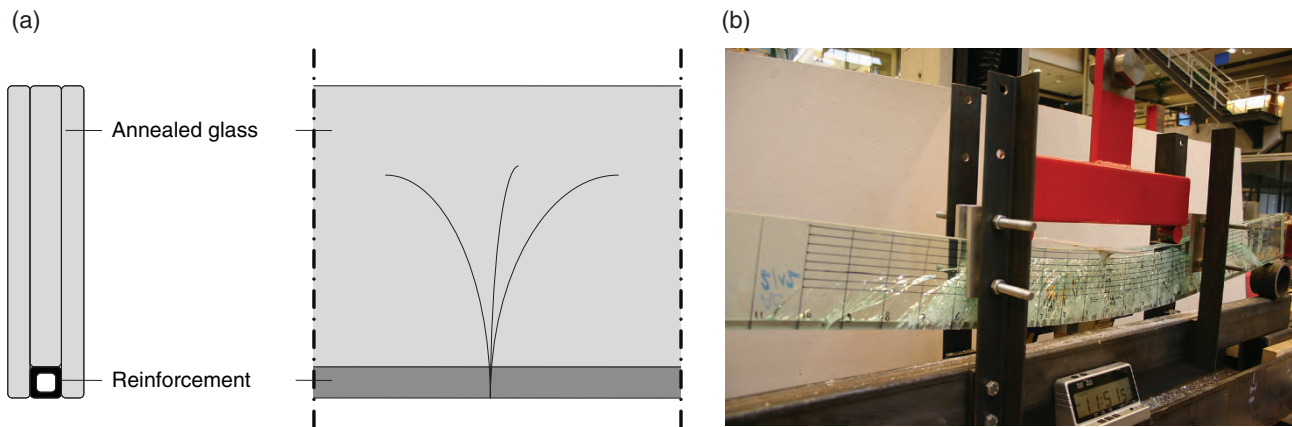


Figure 24 Reinforced glass beams: (a) schematic section and side view, showing principle of post-fracture performance, (b) experimental test demonstrating significant post-fracture resistance [13].

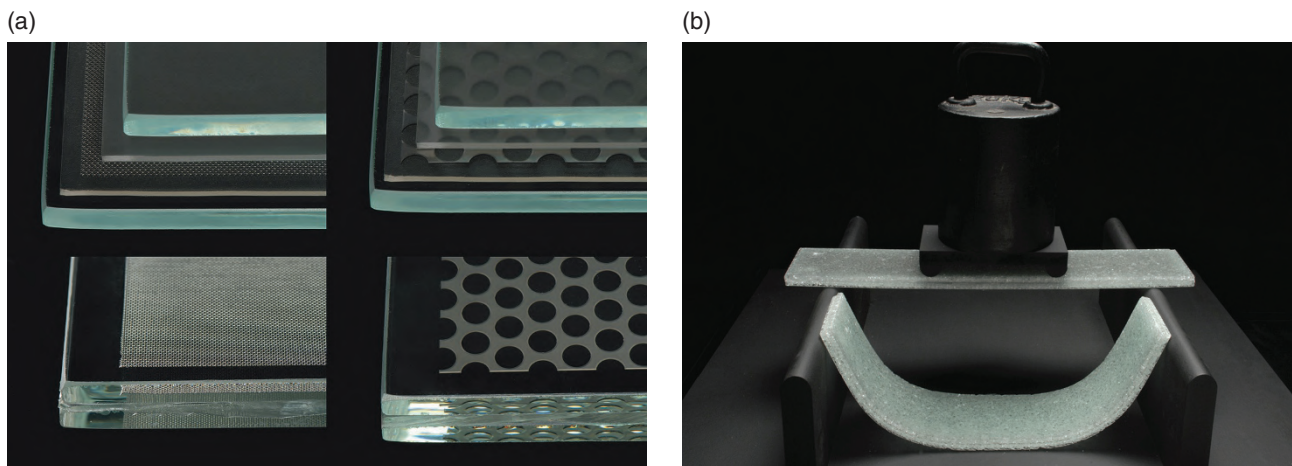


Figure 25 Metal wire mesh or perforated thin metal plate reinforcement embedded in the interlayer of laminated glass [36]. (a) Overview of reinforced laminated glass samples, (b) laminated glass with and without reinforcement.

fracture, the post-tensioning tendons act similarly as the aforementioned reinforcement in reinforced glass beams, thereby providing significant postfracture strength and ductility.

6.6 Smart Glass

A development not directly structural, but nevertheless very important to the use of glass in buildings, is the integration of functionalities to increase performance, mainly related to indoor climate and comfort. Besides selective solar reflective coatings with increasing efficiency, step-less switchable glazing from transparent to opaque is gaining ground [38]. A few years ago, translucent photovoltaic cells on glass were introduced, see e.g. [39]. Now, a window is under development that combines switchability and power generation [40]. Such innovations will further stimulate the use of glass, and are likely to be combined with structural applications as well.

6.7 Chemical Prestressing

A technique that has been known for a significant time and one that may have particular structural use is chemical prestressing. Like thermal prestressing, it results in a compressive prestress in the glass surface. However, this process is based on ion-exchange of surface ions. By submersing a glass sheet in a potassium salt solution at elevated temperature, Na^+ ions in the glass surface are replaced by larger K^+ ions from the bath. This process, known as chemical prestressing, also induces compressive stresses in the glass surface. However, the stress profile through the thickness is different (Figure 10). Very high maximum surface stresses can be reached depending on the submersion time. According to EN 12337-1 [41], the characteristic bending tensile stress of chemically strengthened float glass is 150 MPa (including inherent strength). But the compressive layer is much thinner, and the tensile stress in the inner glass is much lower. Therefore, this prestressing method also induces much less elastic strain energy into the glass than thermal prestressing. As a consequence, chemically prestressed glass does not break into small fragments and can be cut after prestressing.

The thin compressive layer is often considered a weak point of chemically prestressed glass, as it can be penetrated by a scratch, leaving the inner glass (already under tension) exposed. On the other hand, the surface of chemically prestressed glass is harder to scratch, with the Vickers hardness reaching 625 opposed to 550 for annealed glass [42]. Extensive research into the structural behavior of chemically prestressed glass for application in buildings has not been performed. As it is expensive, relatively unknown and comes with the size limitations of

the available salt baths, it is still rarely applied in buildings. Nevertheless, the high tensile resistance in combination with favorable fracture pattern and lack of optical distortion (present in thermal prestressed glass) may instigate more extensive use in buildings in the future.

6.8 Thin Glass

The introduction of smart phones and tablets over the last decade stimulated the development of strong, but extremely thin glasses (typically 0.55–2.0 mm [43]). Trade names include Gorilla Glass by Corning, Dragontrail by AGC, and Xensation by Schott AG. These are not soda-lime silicate, but alkali aluminosilicate glasses. Different production processes are used besides float processes, such as the vertical overflow fusion process. These glasses are chemically prestressed and it is claimed surface compression stresses of over 900 MPa can be obtained, as well as a Vickers hardness of 600–700 [44–46]. Prices and sizes seem to be limiting application in construction, also because for most applications, the panel stiffness will become governing once such extreme strengths are obtained. Then, the thinness is not beneficial anymore. Nevertheless, the possibilities for such glasses are being explored [47]. They may be beneficial particularly in moving building parts such as elevators and retractable roofs.

6.9 3-D Printing of Glass

Additive manufacturing is being explored in all segments of the manufacturing industry, in- and outside of construction. A wide range of materials can be printed. In 2015, an experimental 3-D glass printing facility was presented by MIT [48]. For now, this facility is capable of printing relatively small art-like objects. Although many issues may need to be solved in terms of strength, annealing, optical quality, or size, it is not unthinkable some special glass parts of a structure will be printed in the future.

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9.2

Tempered and Laminated Glazing for Cars

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1 Introduction

Conciliating outside vision with protection against bad weather has long made glass an indispensable material in transportation means. Small flat panels produced by either the crown or mantle processes (Chapter 10.9) were thus early used for the windows of stagecoaches, ships, or train cars. Following the development of direct flat-glass production in the early twentieth century (Chapter 1.4), however, the expansion of the automobile and aircraft industries has put much more stringent constraints on the glass material, first in terms of safety and now of various added functionalities. The goal of this chapter is to describe how these needs are satisfied. We will begin with a brief history of the evolution of car glazing. The various functions of glazing will then be described in relation to vision, safety, heat, noise, information display, and recycling. Manufacturing will then be described in terms of cutting, screen printing, forming, and strengthening. Finally, the new challenges to be met in a near future will be described.

Here, the focus is put on the car market because of its sheer size. But it goes without saying that similar glass products are used in trucks, buses, trains, trams, boats, or aircrafts although the relevant requirements may differ. For instance, whereas a defrosting windshield is desirable in a passenger car, it is absolutely needed in an aircraft cockpit. Likewise, the high-strength requirement for cockpits translate into thicker glazing compared to cars. Glazing is also thicker for boats, for fire-resistance reasons, and even thicker for high-safety, bullet-proof vehicles. On the other hand, styling constraints are of uttermost importance for cars. The manufacturing technologies may also differ: for buses, the glass parts are

much larger than for cars but the series are shorter so that less emphasis is put on throughput and more time can be spent on the forming process. Regardless of such specific features, all these applications are relying on the fundamental advances made in glass science and technology. These are in particular described in the chapters on flat-glass production (Chapter 1.4), physical and chemical strengthening (Chapter 3.12), coloration (Chapter 6.2), electronic displays (Chapter 6.9), and glass recycling (Chapter 9.8), where the relevant background information will be found.

2 A Brief History from the Early Twentieth Century to Today's Huge Market

The first automotive cars had no windows, or windows made of single monolithic non-strengthened glasses, which could be the cause of many serious injuries in case of accidents, but two kinds of safety glazing quickly emerged: first laminated and then thermally tempered glass.

The early history of laminated glass is reported in [1]. In 1903, the chemist Édouard Benedictus (1878–1930) observed in his laboratory that, when accidentally dropped on the floor, a glass flask that had contained cellulose nitrate [$C_6H_8N_2O_9$] was broken but the glass pieces held together, thanks to coated plastic inside the bottle. He filed a patent [2] and founded the Société du Verre Triplex in 1911 for the fabrication of safety laminated glazing. As early as 1919, some of the Ford model T cars featured a windshield made of such safety glass and, according to the National Glass Association, within 10 years the Ford Motors company ordered the use of laminated glass on all of its vehicles. The plastic polyvinyl

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butyral (PVB) $[(C_8H_{14}O_2)_n]$ was invented later in 1927 [3]. It had many advantages over cellulose nitrate, not only in terms of safety but also superior in optics, as less prone to color change over aging so that it was used as early as 1941 in virtually all laminated safety glazing [4].

As for thermal strengthening of glass, it had been known since the seventeenth century through Prince Rupert's drops (Chapter 10.11) but was not applied industrially until 1874 when Francois Royer de la Bastie (1830–1901) quenched hot glass in grease or oil to improve the mechanical resistance of glass objects such as goblets [5]. In Germany, another tempering process better suited to flat panels was invented by Frederick Siemens (1826–1904, cf. Chapter 10.9) who strengthened glass in 1877 by pressing it in between cold molds [6]. Glass tempering with impinging air jets was eventually invented at Saint-Gobain in the 1920s [7], resulting in cost reduction and in improved shape and surface finish compared to previous processes. As a result, this so-called "Securit" glazing took over laminated safety glass in European automobiles in the 1930s – windshield included –, whereas in the United States, it was not until the early 1960s that the use of tempered glass for side window (sidelite) and rear window (backlite) was generalized to ensure lower costs. Tempered glass was not used for windshields in the United States, however, whereas in European countries, safety concerns eventually led in the 1970s and early 1980s to prohibit it and to impose laminated glass instead.

The first automobiles had only flat windows. To improve the design of the most advanced cars, windshields were then made up of two flat parts before it became possible to produce a curved surface as first made in 1947 for the Studebaker Starlight coupe. Curved glazing then became more and more common for all car windows even down to the lower segments of the market. The first car openable sunroof is reported to date back to 1937, but glazed sunroofs only appeared in the mid-1970s.

Today's market for car glass is huge. Glazing for transportation accounted for about 10% (15% in Europe) of the 6 billion m^2 of flat glass produced worldwide in 2010, the overwhelming majority of which having being supplied to automotive original equipment manufacturers (OEM). In the European Union, about 50 factories produce automotive windscreens, sidelites, and backlites. These plants are usually located not far from both car assembly plants (to meet very short delivery time requirements) and primary float lines (to optimize logistics and reduce transportation costs and environmental footprint). In value, the share of automotive glass is even higher, representing around 25% of the global market for the end uses of flat glass, which was estimated at more than 50 billion € in 2010. This figure is expected to double by 2018 [8]. In other words, the secondary transformation industry brings much more

added value to the automotive glazing market than to the two other main end-markets for flat glass, namely, construction building and electronic displays.

3 Glazing Functions

3.1 Vision

Of course, cars have windows because the driver needs – and the passengers want – to see through the cabin that protects them from weather conditions. The ECE R43 European regulation specifies that, as determined from ISO 3538 testing, light transmission be higher than 70% in windshield and front sidelites involved in driving. For the windshield, or at least its vision area, other requirements concern optical distortion and the so-called ghost images. Such images, mostly visible at night, are optical effects caused by the windshield curvature, its oblique inclination, and internal reflections of light at the glass–air interfaces (Figure 1). Optical distortion may in addition arise, especially when laminated windshields are mounted with a low angle over the horizontal or for sidelites when the direction of sight lies at a low grazing angle. Moreover, the optical quality of laminated windshield made with flat glasses from a poorly controlled float glass process can be impaired. The primary float glass surface imperfections (cf. Chapter 1.4) may, after lamination, result in dioptric defects, also causing some distortion in light transmission through the windshield at low grazing angle.

Windshields and backlites have wipers to remove rain droplets or snow flakes and to clean the smudge, dust, or insects that also hinder the visibility. Nowadays, wiper technology can meet most of the usual glazing curvatures and high-speed aerodynamic requirements. Defogging is

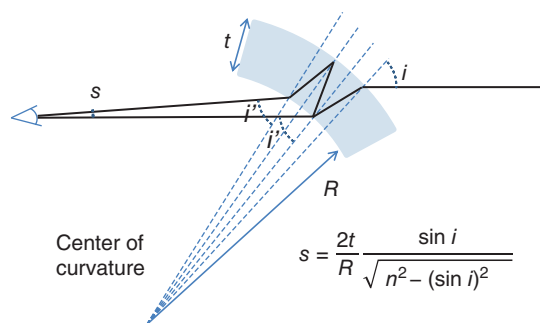


Figure 1 Optical sketch for the formation of the *ghost* image through a windshield of thickness t , with curvature radius R . The driver's eye perceives one ray from a light source, impinging on the windshield under incidence i , and another one, due to internal reflections within the glazing, coming from another incidence, shifted by a small angle s . Source: Adapted from [9].

quite efficiently done with the air-conditioning system of the car, whereas the backlite has for a long time been equipped with printed conductive lines connected to the electric power supply of the car through screen-printed bus-bars (made of the same electrically conductive glass frit as the lines) on which metallic connectors are soldered. Heating laminated windshields, for some few high-end cars, used to be done with very tiny (but still visible) conductive metallic wires, embedded into the polymeric interlayer. Nowadays, windshields can be heated with silver-based transparent conductive thin film [10]. Such heating glazing technology, which ensures much quicker and more comfortable defrosting, is energy-efficient and especially suited for electric vehicles.

Making car windows out of clear plastic without using glass would enable to design more complex shapes and allow for more easy integration in the car body. But current transparent organic materials like acrylic or polycarbonate can hardly be used. They would quickly suffer a loss of clarity from the friction of their surface – especially for the windshield and backlite – against the wipers and from other damages caused by flying dust; and, for the sidelites, during up/down movement. A high enough hardness is a key feature: the ECE R43 European regulation requires passing abrasion tests such that currently transparent polymers with the best available hard coatings can only be used in a limited number of cases, like small fixed quarterlite. It could even be argued that the silicate glass surface strength is hardly sufficient: an examination of the surface of the original windshield from a high-mileage car reveals numerous microscopic craters and scratches that results from very small impacts and from friction with the wipers (Figure 2). These act as

light diffusers that may deteriorate the comfort of driving, even with a clean windshield, especially at night.

There are no specifications for the light transmission of the glazed parts not involved in driving. Actually, passengers may also want to enjoy more thermal comfort and some privacy: these requirements have driven the development by OEM of flat glass with light transmission as low as 10% for a 3 mm thickness. Such a level is obtained through high doping of the usual soda-lime glass with up to a few % of colorants like iron. For retrofit market, application of tinted polymer films is common.

3.2 Safety

Along with vision, safety is a primary requirement for car glass. For tempered parts, it is ensured not only by the higher strength of the glass but also, and more importantly, by the fine dicing produced upon breakage (Figure 3a). The small fragments are indeed much less dangerous than the long and sharp pieces that might otherwise fly or be left salient during a car crash. The ECE R43 European regulation requires that a fragmentation test upon breakage be passed: for a glass thickness lower than 3.5 mm, there must be between 40 and 450 fragments in any 5 cm-sided square. That the fragments tend to stick to one another and stay in place after breakage is a big drawback for tempered-glass windshields, however, which would make vision impossible. In contrast, even though smaller or slower gravels may produce cracks in a laminated glass, their number and size are small enough so that vision is not severely impaired after an impact (Figure 3b). Various other mechanical tests aiming at guarantying safety are included in the regulations: ball

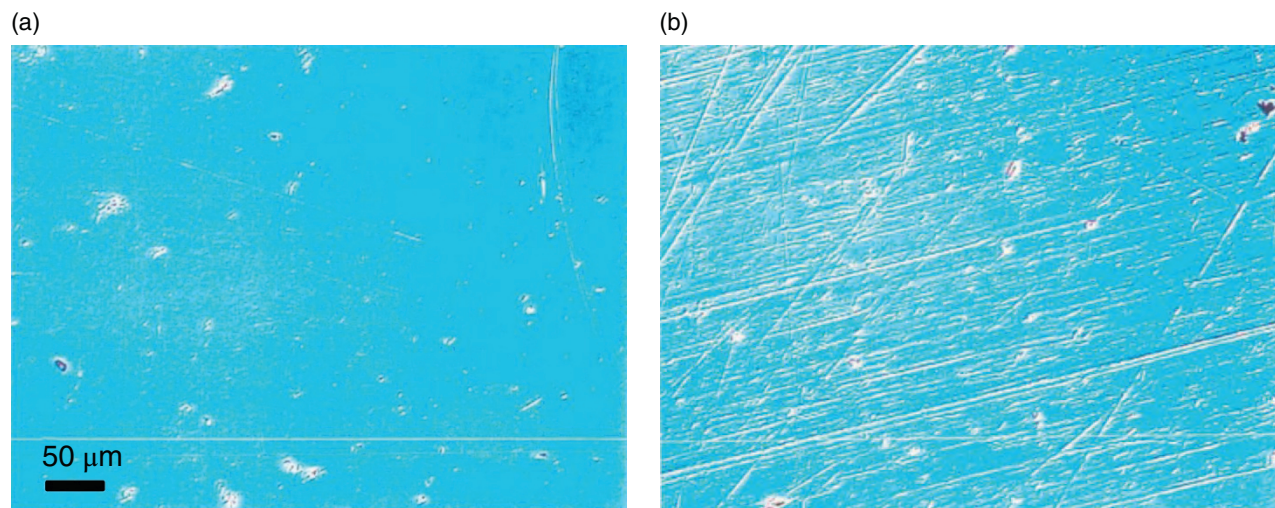


Figure 2 Microscopic craters and scratches on the windshield surface of a 200 000 km mileage car (Nomarski microscopy). (a) Outside wipers area; (b) wipers area. Source: Courtesy P. Lehuédé, Saint-Gobain Recherche.



Figure 3 The differing breakage modes of car glazing: (a) broken tempered sidelite; (b) gravel impact on a laminated windshield, seen from the driver's seat.

drop tests, penetration resistance tests, head-form impact test for assessing brain injury and laceration risks, etc. These tests as well as medical and forensic studies [11, 12] highlight the superiority of laminated glass compared to tempered glass from the safety point of view in case of a car accident and especially of passenger ejection in roll-overs. But laminated sidelites are found only in a limited portion of the high-end segment of the car market because of the cost issue.

A higher resistance to fracture also makes laminated glass superior from a security point of view. A tempered window is a weak point from where thieves can easily steal something in a car. A laminated glazing gives them a much harder job.

3.3 Car Design, Integration to Car Body, and Systems

A nice design is critical for a car to become a commercial success. A key feature of today's designs is the smooth and continuous integration of the glazing. The better-looking integration ensured by the *flush* design became possible more than 30 years ago when the old mounting process of framing with thick rubber gaskets was progressively replaced by the now universal gluing technology whereby polyurethane resins directly bond the glass to the car body. Screen-printed, highly opaque black enamel is provided on the periphery of glass and serves as a mask for the glue for aesthetic reasons and for protection against UV aging. The requirement that the glazing fits to the car as continuously and naturally as possible translates into increasingly tight geometric tolerances for the shape of the complex curvature of the glass and into a thorough control of its optical aspect seen in reflection both from

the outside of the vehicle and under low incidence. To meet these high-quality criteria, the bending process of flat glass has made important progress in the past decades. Still, some of the car designers' ideas are not yet cost-effectively doable with glass, and/or at the required quality level.

Because of its suboptimal aesthetic match to the different car colors, it would be desirable to change the greenish color of the iron-doped flat glass currently used for the automotive application for a more neutral gray color. Moreover, the inside lining of the car would look better, when seen from outside or from inside at daylight, through a glass with a more neutral color. But gray glasses keeping the same anti-solar efficiency are not available at the same low cost as iron-doped glasses.

Design is not the only driver for the ever tighter integration of the glazing into the car body. For car manufacturers, reducing the number of parts and operations on the assembly line is a lever for cost reduction. Therefore, there is a trend for car-glazing manufacturers to bring more value to their products by adding on as much operations, or other materials, as possible, everything that can be done at the end of the glazing fabrication more efficiently than later on the car assembly line. Soldering of electric connectors and deposition of adhesion primers are basic examples. This trend has also led to the development of a number of *post glass* operations at the car-glass manufacturer or at the specialized-part supplier. Periphery joins or other plastics (polyurethane mostly) add-ons are commonly extruded, or injection-molded on the glazing, or at its periphery. The *encapsulation* process involves the injection molding of a polymer trim, shaped precisely to fit the vehicle body, to the periphery of the glazing. It also provides the opportunity to incorporate

additional styling and technological features such as metallic parts (pre mounting), antennas, or sensors. This evolution can go as far as supplying a full system: a back door, an openable sunroof, etc. The case of sunroofs is interesting as it highlights another aspect of glass: as a material, it is hardly stiff enough for the application, especially for complying with the opening mechanism, and upon high-speed driving, the slight inside pressure increase may trigger an upward bowing that is unwanted mostly because of aerodynamics and perceived quality issues. Therefore, metallic reinforcing bars may have to be glued on the glass roofs, or are embedded into the plastic during the encapsulation step. Generally speaking, this lack of stiffness is a concern for parts that are not very deeply curved or cannot be glued on the car body, especially because of the general trend toward larger, panoramic, and thinner glazing.

3.4 Thermal Comfort

One of the primary reasons for using tinted glass for car glazing is to reduce transmission of solar heat to the vehicle interior. Doping glass with transition elements, especially iron, and controlling their oxidation state allow for enhanced absorption in the near-infrared (IR) range (Figure 4). The soda-lime glass composition for automotive applications has been optimized in this way so as to reduce as much as possible the direct solar input. For the windshield, the attainable heat barrier from the glass composition alone is limited because of the 70% visible light transmittance requirement. An even better selectivity is obtained, thanks to the combination of tinted glass with a transparent solar control thin film on one of the two glasses of the windshield, or within the polymeric interlayer. Such high-performance solar-control glazing solutions can reduce heat penetration in vehicles by more

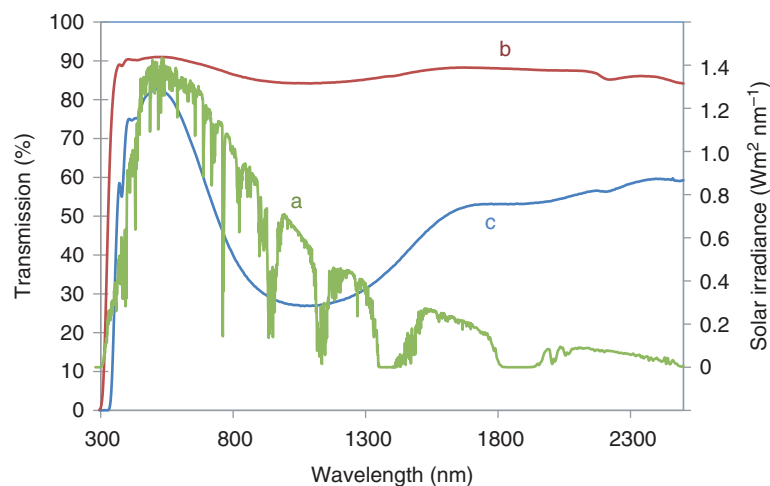
than 25% and the interior cabin temperatures by 7 or 8 °C [13]. This technology is especially valuable for electric vehicles, for which savings on the energy consumption from the air-conditioning system are welcomed, as they readily translate into an increase of the vehicle range autonomy. For nonelectric vehicles, it is also interesting as any reduction on the load work on the air-conditioning is a way of lowering the CO₂ emissions.

There is also an issue with cold climate comfort: cars tend to have larger and larger panoramic glass sunroofs, the inner side of such a large glazing takes advantage of a low-emissivity coating (Chapter 6.8), which can help reduce an otherwise too strong radiative cooling from the inside.

3.5 Acoustic Comfort

The noise perceived in a car may originate not only from the engine, power train, and tire friction with the road but also from aerodynamic interactions with the car body. Glazing is a preferred path for noise ingress into the vehicle interior. For example, at high speed, the wind turbulent pressure fluctuations against the glazing make it radiate noise inside the car. On the other hand, reductions of the car fuel consumption and greenhouse gas emission are drivers for more lightweight cars, and more lightweight glazing in particular. This makes it more difficult to improve acoustic comfort in the car. From an acoustic standpoint, a laminated glazing performs better than a monolithic tempered glazing of the same weight because some vibration damping takes place within the PVB itself, which can even be enhanced further (Figure 5) with special multi-ply high-damping *acoustic* PVB [15], resulting in insulation improvement of about 5 dB, which is quite noticeable to the ear [16].

Figure 4 Effect of iron doping on the transmission of near-infrared radiation by a 3.85 mm thick glass: (a) solar irradiance; (b) regular glass; (c) auto glass (about 0.6% Fe_xO_y). Source: Courtesy O. Cintora, Saint-Gobain Recherche.



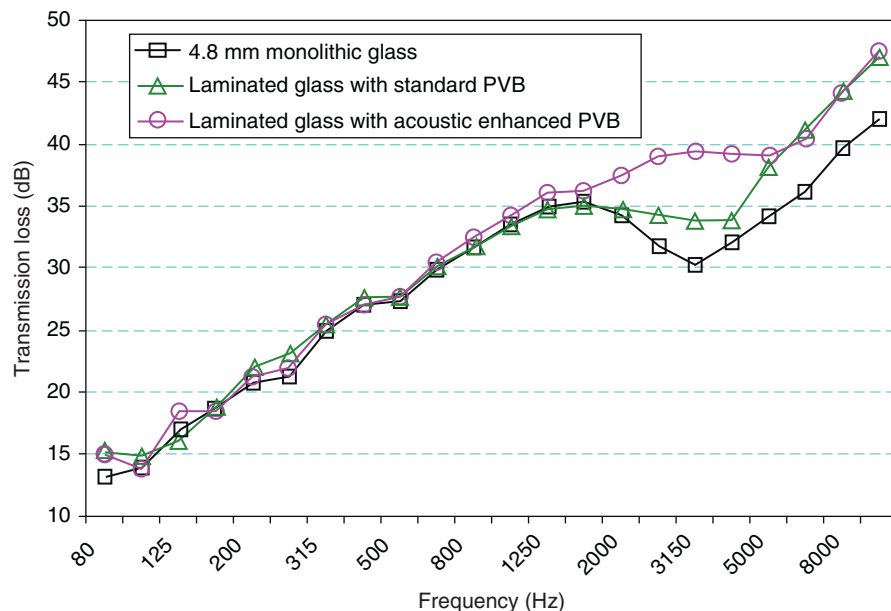


Figure 5 Effect of glass lamination with PVB on sound-transmission loss at 20 °C for a panel size is 47 × 74 cm, from [14].

3.6 Communication, Information Display, and Other Advanced Functions

Nowadays, cars are connected objects so that the glazing has to be a window not only for visible light but also for electromagnetic waves carrying information at the frequencies relevant to radio sets, GPS, telephone, or Wi-Fi, and also to remote-controlled garage doors or toll barriers. Antennas are screen-printed on the backlite, on top of the heating lines, or on other glazing and become virtually invisible to improve the vehicle's profile and reduce noise from wind or vibrations. Glass has fitting dielectric properties ensuring a very good reception quality and a broad bandwidth. On the other hand, windshields featuring electrically conductive transparent thin film may be problematic, which is why a small portion of the glass surface is better left without any film.

Projecting information from the dashboard on the windshield, so as to make it visible by the driver head up, as an image focusing at some distance ahead of the car, has been existing for quite a long time. The head-up display technology originates from the military aircraft industry. The quality of the image is improved, thanks to a special wedge-shaped PVB interlayer [17] in order to eliminate the ghost image issue. This functionality is still limited to a small segment of the automotive market, but in the near future, the windshield will more and more have to be compatible with, or even used as, an information display device for the numerous systems that are now available in order to provide assistance to the driver, especially at night.

3.7 Recycling and Sustainability Issues

Between eight and nine million tons of end-of-life vehicle (ELV) waste is generated each year in the European Union [18]. Glass amounts approximately to 3% of the total weight of a car. Disposal in landfill of waste glass from cars will not be permitted in most European countries as the 2000/53/EC European ELV directive is implemented. In principle, glass is an infinitely recyclable material, but the process of dismantling a car and sorting out the different materials is complex and difficult. For glazing, the strength of the glued bonds to the car body becomes, at that stage, somewhat of an issue. Removing the metallic parts, connectors, etc., is not easy and even more so, separating the PVB that, by the way, is a rather valuable scrap by itself, also susceptible of a recycling process after purification, melting, and reshaping. Even though a limited amount of PVB remaining on the glass fragments is acceptable as it will be burnt in a glass-melting furnace, the as-obtained glass cullet also needs to be refined to be melted again. Still its quality is insufficient for being reused in significant amount in float glass furnaces. It would be compatible with lower-grade glass applications, such as glass wool and probably bottle manufacturing, but the cost of such refined glass cullet from ELV waste remains high. In addition to the above technical challenges in dismantling and separating car glass from other materials, there is also the need to organize cost-efficient supply chains and markets from the thorough collection of ELVs to the mass production of refined glass cullet from ELVs and, eventually, transportation to

glass melting furnaces. But these are high barriers still to overcome before viable circular economic processes can be fully developed.

Besides setting targets for the recycling of ELV, the same European directive also prohibits the use of heavy metals in auto parts. Lead, which was present in the glass frits for enamels and in the alloys for the electrical connection soldering, is no longer used in car glazing. Lead-free technologies have been developed for these applications.

4 Manufacturing

4.1 Cutting/Edge Machining

Car windows are made out of standard size soda-lime silicate glass rectangular panels from the float process, approximately 3 m × 6 m, which are further cut down to smaller rectangular shapes fitting the size of the windows. The big panels may also have previously received any functional thin film coating that must survive the subsequent manufacturing steps. The thickness is around 3 mm or less for glass to be laminated. The glass-cutting process is automated. A sharp tungsten carbide or diamond wheel is first moved onto the glass surface along the curved periphery of the piece to be cut, so as to create a continuous blind surface crack a few hundreds of microns deep. Following scoring, a breaking bar moves upward, from underneath, and drives the propagation of the cracks along the previously scored line under double-torsion loading. A cutting oil is used during scoring to ease the whole process, as it prevents moisture from the environment from interacting too much with the cracks and, thus, from attenuating the scoring residual stress field [19]. The outer part is trimmed, thanks to additional straight lines scored up to the edges of the initial rectangular plate in the main directions of the curved line to ensure trims as straight as possible for easier breaking. Trims are recovered to be recycled into a float furnace.

Coming right after cutting, edge working serves a dual purpose: car glazing generally has apparent edges that should not be sharp for safety and aesthetic reasons. A grinding wheel, featuring diamond grits held together with a metallic bond, whose edge has a concave C-shape, runs along the edge until the desired shape and smoothness are obtained. A grinding fluid is used for cooling, lubricating, and continuously cleaning the wheel. Drillings are also done according to the customer's requirements, for example, for a movable sidelite or for the wiper axis of the backlite. Finally, the parts go through a washing machine to remove all the remaining debris and traces of cutting oil.

4.2 Screen Printing

The aforementioned black enamel is a paint obtained by mixing a low-temperature melting glass frit, mineral pigments, and an organic medium. Its rheology is adapted for a screen-printing process (serigraphy). As said, the black enamel serves a design purpose and protection of the gluing. The same screen printing step is also used to print some mandatory information, car manufacturer logo, and details about the glazing specification and production traceability. The freshly painted parts have to be dried online in a continuous tunnel oven. When required, a conductive circuit (another frit paste, highly loaded with silver powder) is also screen-printed on top of the black and on the glass, on the "tin" side of the original float glass. All the remaining organics are removed during the following heating step while the enamel is fired.

4.3 Heating

The glass is heated up to about 650 °C, i.e. about 100 °C above the glass transition, to lower its viscosity down to about 10⁹ Pa·s. This heating takes place continuously in tunnel furnaces. For tempered glass, the parts are conveyed on rollers whereas for laminated glass, they are conveyed pairwise, one on the top of the other, on a moving trail of peripheral frames (Figure 11a). Although the physics of flat glass heating is complex, a very good control of heating is critical for the following forming and strengthening steps. As glass moves, it is exposed on both sides to the IR energy of radiant emitters covering the inner walls of the furnace. Because of the semitransparency of glass in the IR range of the emitters' spectrum, the heat-flux density absorbed strongly depends on furnace temperature and on the thickness and iron content of the glass [20] (Figure 6). The situation is complicated further by the enamel, whose IR properties differ from those of the bare glass and, when present, by any thin film coated on the glass. Radiation is the main contributor to the heating, but heat convection is not negligible (low-emissivity thin-film coated glass may take advantage of reinforced convection heating furnace). Heat transfer by contact with the conveying rollers, which may induce transient glass bowing on the hot rollers and conveying issues in the furnace, has also to be considered. Heating must generally be as homogeneous as possible for tempered parts, but is purposely nonhomogeneous for laminated parts to meet the forming requirements.

4.4 Forming/Strengthening of Tempered Parts

The physics of glass thermal tempering and the associated building up of residual stress in flat glass were understood in the 1970s [21]. Upon symmetric cooling, the

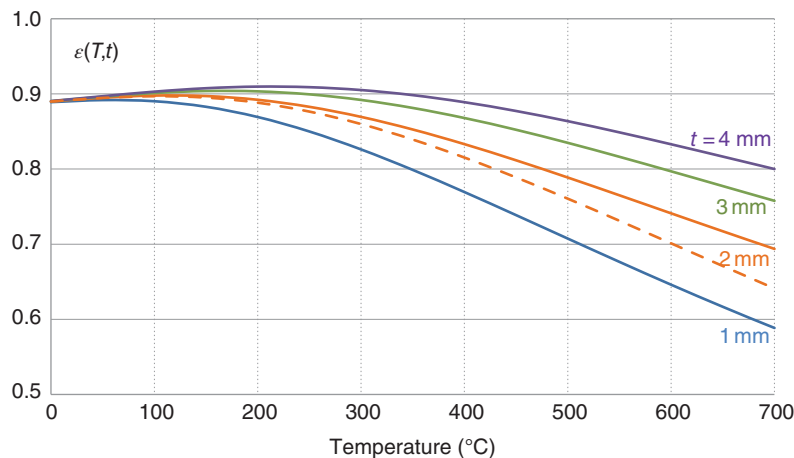


Figure 6 IR absorptance (resp., emittance) of flat glass for different thicknesses t , as a function of furnace (resp., glass) temperature T . Plain lines: 6000 ppm total iron oxide content. Dotted line: 450 ppm total iron oxide content. Source: Courtesy D. Mélite, Saint-Gobain Recherche.

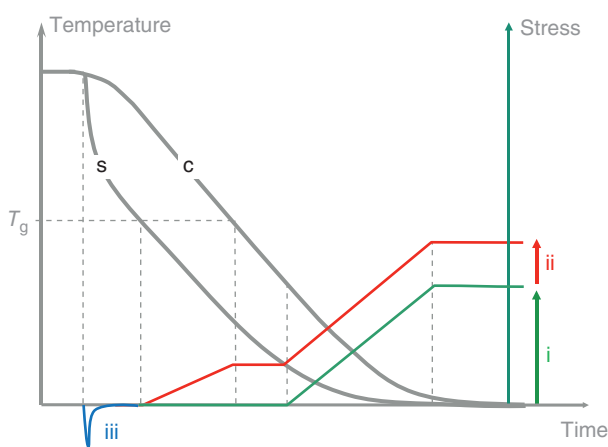


Figure 7 Sketch for the genesis of tempering stress upon cooling of a glass plate. (s) surface temperature; (c) core temperature; (i) thermoelastic contribution stress; (ii) structural contribution; (iii) initial transient tensile stress. Source: Adapted from [20].

temperature profile across an initially uniformly hot plate quickly becomes roughly parabolic. The parabola then shifts to lower temperatures without changing much its shape until it flattens when room temperature is approached. If the glass is fluid enough when the parabolic temperature profile takes place, the initial phase of the cooling is not accompanied by any thermal stress. Stress would start to appear only when the temperature parabola gets flattened: the core tries to shrink more than the surface, resulting in the well-known surface compressive stress compensated by a tensile core stress. However, according to in situ photoelastic experiments made during cooling through the glass transition range [22, 23], a transient tensile surface stress is observed at the very beginning of the cooling and some compressive surface stress is observed as soon as the core temperature reaches the glass transition range (Figure 7). The former observation is a viscoelastic thermal shock stress, which is all the

more significant that the initial fluidity is low: this explains why too low an initial temperature results in a lower final tempering stress and in frequent breakage at the beginning of tempering. The latter is explained by the steep change in thermal expansion when the glass undergoes the glass transition; this *structural* contribution to the tempering stress is higher for thicker panels whose glass transition takes place at a higher viscosity in view of a lower cooling rate. Nevertheless, the obtained stress profile is roughly parabolic, parallel to the steady-state parabolic temperature profile upon cooling. The magnitude of the residual stress is proportional to the maximum core-surface temperature difference, which scales with the intensity of the cooling and with the glass thickness.

These features explain (i) why it is necessary to heat the glass well above the transition temperature to start with a fluid enough glass; (ii) why the residual stress does not increase further with an initial temperature higher than a certain value, (iii) why glasses with low thermal expansion coefficients, e.g. borosilicates, are unfit for thermal tempering; (iv) why tempering thinner glass requires a larger cooling rate. For car-glass tempering, the typical heat exchange coefficient with impinging air jets must be of the order of $500 \text{ W m}^{-2} \text{ K}^{-1}$ or more and be as homogeneous as possible over both glazing surfaces. These conditions are achieved in carefully designed *quench boxes* where arrays of nozzles, supplied with a high flow rate of cold air from big fans, are blowing at a high speed from a controlled distance onto the glass surfaces. For large parts and thinner glasses, quench boxes must be carefully designed to ensure an efficient evacuation of the very large amount of blown air, which would otherwise become a limiting factor for the heat exchange coefficient or its homogeneity over the surface.

Thermal tempering of thin glass is made even more difficult for other reasons. First, a larger residual stress is required to obtain the same fragment size in a thin glass

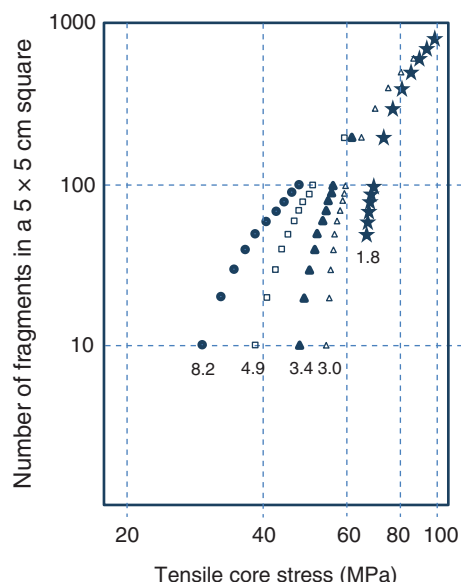


Figure 8 Fragmentation of tempered glass as a function of tensile core stress. The numbers refer to the glass thicknesses (mm). Source: Adapted from [24].

as in a thick glass (Figure 8). The size of the fragments comes from the bifurcation length of a through thickness crack, which is the length at which the stress intensity factor for such a crack reaches a critical value. But this stress intensity factor does not depend only on the stress magnitude but also on the thickness itself as explained, for instance, in a recent model of the fragmentation process in tempered glass [25]. Second, as already stated, the structural contribution to the tempering stress is lower for thinner glass. Third, the minimal fluidity needed at the beginning of the cooling is larger because of the

higher cooling rate required. Hence, tempering thinner glass requires a higher initial temperature. But to convey, manipulate, and shape a very hot and thin glass while preserving the geometric and surface quality is a real technological challenge. In industry, it is hardly possible to temper soda-lime silicate glass thinner than 2.5 mm at the required yield and optical quality level. On the other hand, there is no real need for developing further the technology of thermal tempering of very thin glass for automotive application, in spite of the weight that would be saved, since such a thin monolithic glazing would have quite a poor acoustic performance.

The forming of quasi cylindrically shaped tempered sidelite is done online, at the same time as the tempering: upper and lower straight rollers at the exit of the heating furnace are conveying the hot glass trough the quenching boxes without interruption. The outside rollers' bed has the desired cylindrical shape, driving the glasses upward. The forces applied to the glass as its moving direction changes is enough to bend the glass as it is simultaneously quickly cooled down by the air jets [26]. One does conveniently shape adjustments by playing with the non-symmetry of the cooling. This simultaneous forming and bending process is very efficient from an industrial point of view, as the continuous production of sidelites at a rate of more than 20 parts per minute is achievable (Figure 9).

More complex-shaped sidelites and backlites require either sag- or press-bending: before being transferred in the quenching boxes, the hot glass is taken from the rollers and supported at its periphery by a ring mold, while the action of gravity gives the shape. It can also be pressed against a generally convex upper mold. Special contacting materials have to be used to cover the molds, which lie either inside or outside the furnace. The shaped glass is

Figure 9 Sketch of a machine for shaping and simultaneous tempering of sidelites. (10) furnace; (9) conveying roller; (4, 11, 13) shaping rollers; (25) blowing boxes. Source: From patent FR 2549465.

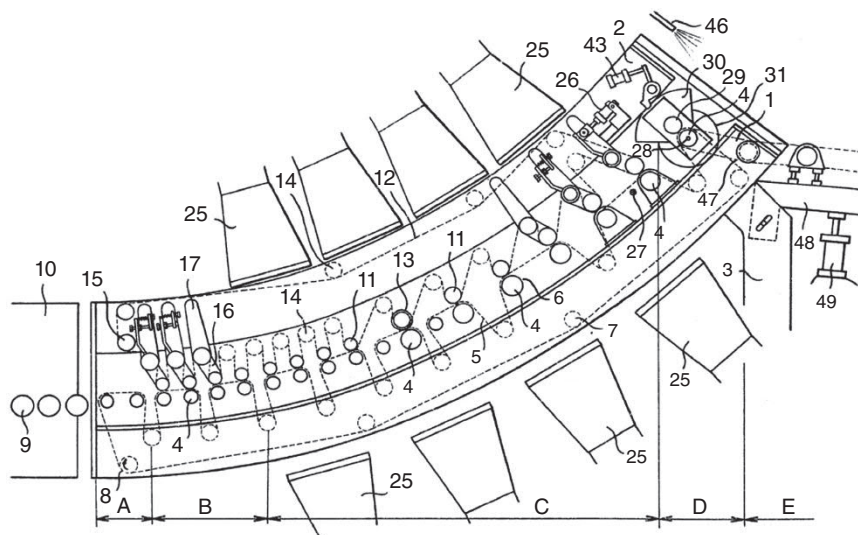




Figure 10 Strain pattern caused by an anisotropic heterogeneity of the residual stress, visible under certain natural light conditions, as a mottled appearance of the tint of the glass; here on a tempered backlite.

then moved and tempered into appropriate quenching boxes. During air blowing, the part is supported on an air-permeable peripheral tool to ensure proper tempering of the edges as well. The tempering tool is given an oscillating lateral movement during air blowing. Because of a small spatial variation of the heat exchange coefficient under the air nozzles of the quench box, there is a slight variation of the degree of tempering. In turn, a slight photoelastic effect may be observed when the glazing is seen under the slightly polarized natural light from a clear sky, as a small portion is reflected back in the direction of the viewer, on the inner glass surface and hence undergoes a slight change of polarization direction upon reflection close to Brewster [27]. The angle at which the glazing is seen, hence its inclination on the car body, has an influence on the perception of this undesirable “strain pattern” of tempered glass (Figure 10), but the lateral back and forth movement of the part in the quench boxes mitigates this effect.

4.5 Forming/Strengthening of Laminated Parts

As already stated, the two glasses for a windshield are heated up together at a temperature above 600 °C, one lying on top of the other and supported on their periphery on an annular mold. An anti-sticking agent is provided in between the two to prevent any risk of sticking when the glasses get softened into the furnace. The force driving the shaping comes from gravity (sag bend) or, once softened enough, from mechanically pressing against another mold (press bend). One key feature of the process for forming of glasses for the manufacturing of laminated parts is the simultaneous deformation of the two glasses. This ensures a better control of the difference of shapes between the two glasses, which is critical for a good

product after lamination. The spatial distribution of the radiative heating power in the bending furnace is purposely nonhomogeneous, and the annular mold may also feature movable parts (Figure 11b) so as to modify the supporting conditions while sagging, in order to obtain the desired complex shape, which is not the one that a homogeneously heated glass would take upon natural sagging while supported on its periphery on simple frame.

The control of glass heating for the forming of windshield is a critical matter when, as usual, the two glasses do not have the same thickness or the same IR absorption (not the same color) or have a low-emissivity coating. Moreover, once the shape is obtained, the glasses have to be cooled down in a controlled way. As the glass at the end of the forming step is thermally nonhomogeneous, a noncontrolled cooling down would produce residual stresses as in thermal tempering. But in this case, the self-equilibrated tensile and compressive stresses would not be so much distributed across the thickness than laterally (membrane stresses). The areas undergoing the glass transition later during cooling would end up under tensile residual membrane stress. The effects could be detrimental to the gravel-impact resistance of the final windshield, as small benign cracks from the gravel impact might grow, even subcritically, under the permanent tensile residual stress. A proper control of thermal history during cooling down after forming is thus required to circumvent this issue.

At the outlet of the furnace, the two sheets of glass, now in their final shape, are separated, washed, and dried. Then a layer of PVB is inserted between them. This operation must take place in a clean room to prevent any dust from being trapped in the laminate and from becoming an optical defect in the final product. The art of manufacturing an optically clear laminated glass is essentially that of removing air bubbles in the assembly, and preventing them from coming back later upon aging. To do so, one has to remove as much air as possible from the sandwich before the final bond between the glass and the polymer is set. This is the role of a preliminary step, in which the slightly heated laminate is squeezed (for example, mechanically in between *nipper* rollers, or by processing in bags under vacuum) allowing as much entrapped air as possible to get out through the edges. The surface of the raw PVB films intended for laminate glazing fabrication may intentionally be made rough by the supplier to facilitate air evacuation. At this step, a provisional glass–PVB bond is created, but the final bond will not be given until the end of the next step, which is autoclaving. Inside the autoclave, the temperature rises up to 140 °C and the pressure up to 12–13 bars. This is enough to dissolve any remaining gaseous inclusions into the PVB and to create the final adhesion between the glass and PVB. At the end of this step, the windshield is perfectly

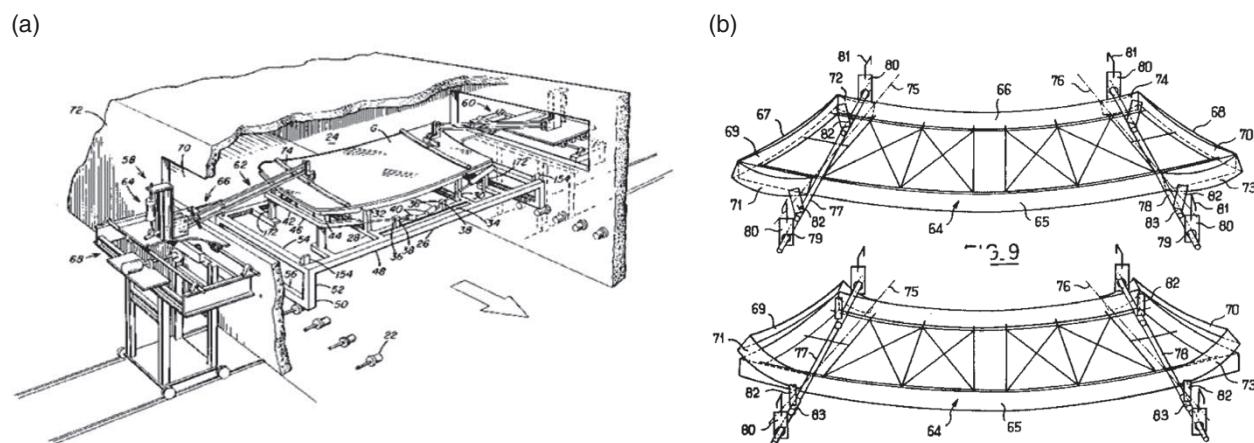


Figure 11 Sketch of tunnel furnace (a) and tooling (b) for windshield shaping. *Source:* From patents US 4804397 and US 5167689.

transparent and passes all the mandatory optical, mechanical, and aging tests.

4.6 Final Operations

The glazing manufacturing process ends with inspection and packaging before delivery to the car manufacturer. Prior to that step, however, there may also be some additional finishing operations: deposition of an adhesion primer on the periphery for to-be-glued parts, metallic connection soldering on the screen-printed bus bars, or apposition of different kinds of brackets for rear-view mirror or sensors. Some of these steps may take place prior to the autoclave in case of windshields. And also, as already explained, injection molding or extrusion of plastics joints or frames at the periphery, including metallic parts, is also done on demand.

5 Perspectives

Glass, as a material, has shown a remarkable ability to accompany the formidable development of the transportation industry, as particularly well exemplified by the extreme conditions that train and aircraft windshields can withstand, thanks to quite thick laminated glazing including very strong, chemically tempered glasses [28]. Glass has also successfully met tougher and tougher technological demands from car manufacturers in terms of volumes, quality, and cost efficiency, while satisfying the needs of the final customers in terms of design and functionalities.

Further progress is nonetheless desirable in various respects. Research is ongoing to modify the car glazing surface so as to make it water and smudge repellent in

a durable way under all driving circumstances. This remains a very difficult challenge. In addition, electrochromic glazing, whose light and solar heat transmission can be actively controlled, and other actively controlled privacy glazing should find their place in the car market, once their cost will be sufficiently brought down. Further acoustic comfort improvement is also needed. In the future, active noise reduction systems might somewhat open the acoustic lock on the path to more thin and lightweight car glazing. Yet another important field is the incorporation of ultra-thin, high-quality organic-light emitting diode (OLED) displays (Chapter 6.9), which will enable GPS map, rear views, or other images to be displayed in some nontransparent parts of the windshield. Likewise, opaque portions of glass sunroofs will integrate an inside lighting function, or even this function will be integrated in the transparent area, thanks to transparent OLED flat lamps. The inside face of car glazing is also expected to incorporate touch-control functions whereas transparent sensors will be integrated into the glazing: rain sensors for active control of wipers, light sensors for the active control of the optical properties of the windshield, for instance, for the provision of an automatic anti-glare function.

As electric and hybrid vehicles' share of the market increases, photovoltaic cells integrated into glazing, especially into sunroofs, allowing for electricity generation, are probably going to be more common. Additional challenges ahead are the need for curbing the CO₂ emission, and the trend toward electric vehicles and lightweighting. These are strong drivers for ever thinner glass. How is car glass going to reinvent itself to respond to these trends, while meeting safety, comfort, and cost requirements? At the same time, how is it going to integrate additional new functionalities? Innovative associations of different kinds of glasses or with other materials might be needed

for these exciting developments. But then, this will complicate further another big challenge ahead, which is recycling.

As a matter of fact, technological development is not the only reason why glass certainly has a bright future in cars. More than ever, perceived qualities, emotions, and environment consciousness are driving the car market. Glass is a perfect fit in that respect: this is a very old material that final customers have always been crediting with many qualities like purity, durability, and recyclability.

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9.3

Stone and Glass Wool

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1 Introduction

With current concern over either climate or population growth, environmental protection has become a critical issue, so new technologies are rapidly emerging for energy generation and saving and, thus, reduced CO₂ emissions. Insulating materials against cold and heat play a crucial role in this respect. Among them, mineral wools, made up of silicate fibers, are most important thanks to their outstanding thermal and acoustic insulating abilities combined with non-flammability or even superior fire barrier functions. In terms of chemistry, raw materials, and production techniques, three families can be distinguished, namely, stone, glass, and slag wool, the first two being by far predominant. Depending on their functions and temperature stability ranges of service, they are used for a wide variety of applications. In all cases, however, the term *mineral* might be misleading because the fibers are not crystalline but highly vitreous as a result of hyperquenching performed at cooling rates higher than 10⁵ K/s. Hence, these glasses have higher fictive temperatures and higher potential energies than their bulk glass counterparts (Chapter 3.8).

Silicate glasses are not by themselves good thermal insulators as their thermal conductivity (K) at room temperature is typically on the order of 1 W/(m K) (Chapter 4.5). Air, in contrast, has a K value of only 0.025 W/(m K) at 283 K, which is why all efficient insulating materials rely on encapsulation of large fractions of immobile air in the form of non-connected microcells to achieve appropriately low thermal conductivities. In this respect, the fundamental advantage of mineral wools, compared with natural products, is that their fibers can be

engineered to decrease the thermal conductivity from a common 0.045 down to the very low value of 0.032 W/(m K) at 283 K for densities typically ranging from 20 to 80 kg/m³ depending on chemical composition, density, fiber diameter and orientation, and maximum temperature of use.

Stone wool has a very long history if one takes into account the so-called Pele hairs hydrodynamically drawn in air during volcanic eruptions from fluid basaltic magma (Chapter 7.2). Man-made stone wool, slag wool, and glass wool have in contrast much more recent origins since they were first produced in the 1930s as more efficient substitutes for cellulose fibers. In recent years, there has been a rapid development in mineral wool production technologies. This evolution is being driven by energy savings, fast technological developments in many relevant fields, and increases in both production capacity and market demands and also by an increasing diversity of the raw materials used. In parallel, understanding of the properties and fiber formation of mineral wool has greatly improved, which is allowing technologists to tailor the performances of insulating wools for different applications and to design and control the production processes of fibers for achieving high-quality products along with high-energy efficiency.

The production technologies and the properties of mineral wool are presented in several books [1–3] and articles [4–6], whereas there is no need to tell again the history of these processes [7]. Spinning of these materials is an enormously complicated process since it is controlled by intrinsic factors of the melt such as viscosity near the liquidus temperature, surface tension, and crystallization tendency, as well as by the extrinsic factors of the processes themselves such as spinning speed, air-jet flow rate, temperature field, external cooling condition, geometry of spinning devices, and melt-metal contact

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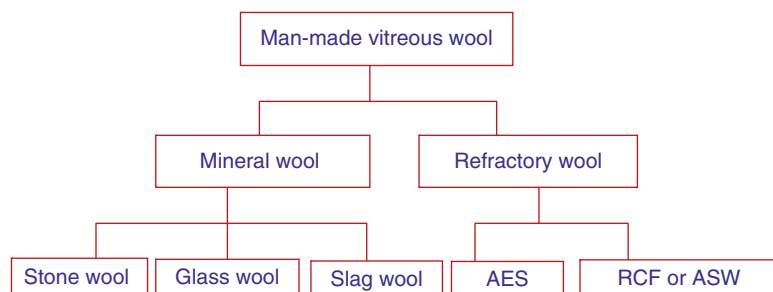


Figure 1 Classification of man-made vitreous wool used for insulation. AES, alkaline earth silicate wool; RCF, refractory ceramic fibers; ASW, aluminosilicate wool.

surface. These aspects will not be discussed here. The focus will be instead on fundamental knowledge about fiber spinning processes and fiber properties of stone and glass wool, such as melt viscosity, thermal history, high temperature stability (HTS), elastic moduli, hardness, and tensile strength. Finally, attention will also be paid to high-temperature applications of these products and to the environmentally sensible issue of fiber biodegradability.

2 Classification of Man-Made Vitreous Wool

All types of commercially important man-made vitreous wool are silica based, i.e. they contain $[\text{SiO}_4]$ units as network formers along with various amounts of oxides of boron, aluminum, alkaline earths, alkalis, iron, and zirconium, which are added to enhance the manufacturing process or the product performance. The general classification of man-made vitreous wool includes two subsets: mineral and refractory ceramic wool (Figure 1). Stone wool is usually prepared from raw materials such as recycled materials, volcanic rock (typically basalt), and the olivine $[(\text{Fe,Mg})\text{SiO}_4]$ and dolomite $[\text{CaMg}(\text{CO}_3)_2]$ minerals, whereas slag wool is synthesized primarily from blast-furnace slag ([1], Chapter 7.3) and glass wool from sand, recycled glass, limestone, soda ash, and other chemical additives (Chapter 1.2).

The chemical compositions of four typical examples of man-made vitreous wools are listed in Table 1, where the presence of low- and high-alumina products is to be noted for stone wool. The chemical compositions of both glass and slag wool are also displayed in Table 1. Despite being termed *slag wool*, this wool is also highly glassy since it is hyperquenched during fiber formation.

Man-made vitreous wool fibers are manufactured with a variety of processes based on the attenuation of a thin stream of molten inorganic oxides at high temperatures. Depending on the process, they are produced as discontinuous fibers of variable lengths and diameters that are intimately tangled. This feature distinguishes *wools* from

Table 1 Examples of mineral wool compositions (wt %).

Oxide	Stone wool		Glass wool	Slag wool
	High Al_2O_3	Low Al_2O_3		
SiO_2	36–42	50–52	60–70	33–42
Al_2O_3	17–24	>3	3–7	11–20
TiO_2	0.5–3		<0.1	
Fe_2O_3	4–11	<1	<0.5	0–2
CaO	14–25	28–30	5–13	35–42
MgO	2–12	8–12	0–5	6–13
Na_2O	0–6	0–4	13–18	0
K_2O	0–6	0–2	0–2.5	0
B_2O_3	0	0	3–7	0

fibers (cf. Chapter 1.6), the latter being continuous or discontinuous.

3 Fiber Spinning Technologies

Two main spinning technologies are used for the production of vitreous wool fibers. Stone and slag wool fibers are traditionally produced with a cascade spinning process (i.e. external centrifugation), whereas glass wool is produced by rotary spinning (i.e. internal centrifugation). Besides, other fiberizing processes such as flame attenuation and air blowing are mainly used for production of high-temperature insulation wool and thin insulation wool fibers.

With the exception of those used in high-temperature applications, the newly drawn fibers are immediately coated with an organic-binder spray before being collected on a conveyor belt as a continuous blanket. When it has reached a given thickness, the blanket enters a curing chamber for binder polymerization and is finally cut into the requested specific dimensions and compressed to some extent to reduce the volume of the product as much as possible for transportation and storage before use.

The main function of the binder is to hold the fibers together. It is often a phenol-based resin that typically can account for up to 1–10% of the mass of the final product. But alternative binders such as acrylic binders or binders based on sugar are being introduced because of increased concern on chemicals such as formaldehyde, which is a component of the phenol resin.

3.1 Cascade Spinning Process

The principle of the cascade spinning process is sketched in Figure 2a. The starting melt for the fiber is produced in a coke-fired cupola or in an electric- or gas-heated furnace with capacities of approximately 100–400 ton/day. Depending on capacity, each melting unit has from one to three spinners, which consist of up to four water-cooled alloy wheels (circumference: approximately 0.5–1 m) with parallel axes rotating at a speed of 5000–8000 rpm. At a temperature of approximately 1400 °C, the melt with a very low viscosity of about 2 Pa·s is imposed onto the rotating spinning wheel. This transfer causes a sharp temperature drop and, correlatively, a viscosity increase [3, 4]. While some fibers are spun off by the centrifugal force from bulge-shaped instabilities at the wheel-melt layer, the rest of the melt falls on the next wheel for fiber spinning.

Upon wheel rotation, bulge-shaped instabilities occur on the surface of the melt film, which are caused by a combination of the high acceleration field of the wheel and an air jet. The bulges remain connected with the melt

film via surface tension and viscous forces [4], but they are eventually torn off to give rise to a melt droplet. It is the narrow melt ligament connecting a droplet to its bulge that is stretched as a fiber under the centrifugal force of the wheel. The fiber breaks when the stretching stress exceeds its tensile strength, which happens for a mean diameter of 2–5 μm and a mean length of up to 5 mm, while the remaining droplet is frozen in as a *shot*. Because shots account for 25–40 wt % of the raw stone wool, they are for the most part separated from the wool by gravity right after fiber spinning to be melted and fiberized again, the rest being left in the wool.

The properties of final products are determined by numerous factors, which include the wool packing structure, binder distribution in the product, fiber diameter and length, fiber spatial distribution, and shot fraction. Because the efficiency of fiber spinning depends on viscosity and melt homogeneity, melting in the melting units must be performed at a high temperature of about 1500 °C for at least half an hour. In addition, it is essential to maintain a stable melt flow to the spinner and to control properly the impingement point of the melt flow on the first spinning wheel to optimize spinning and improve wool quality by reducing in particular the shot fraction. In this respect, the air-jet rate around the spinner wheels is an important feature influencing shot formation [4].

Reducing the shot fraction of the raw wool actually is a crucial point to increase the efficiency of the process. For this purpose, experiments and numerical modeling have

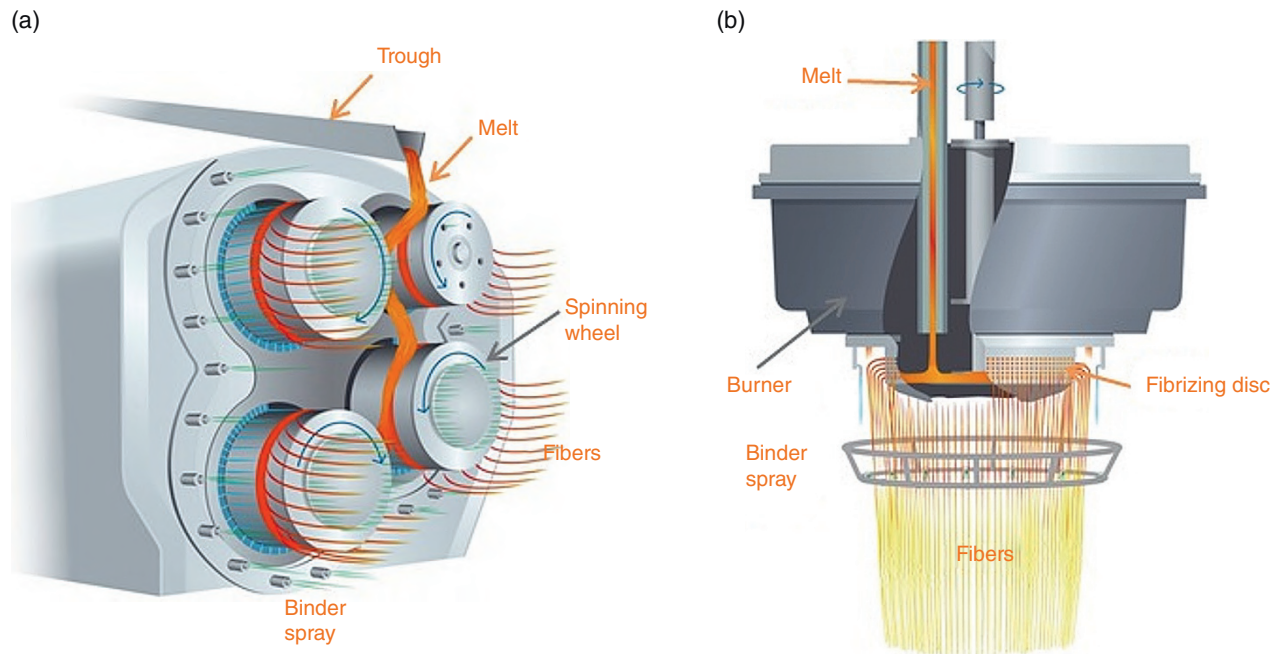


Figure 2 Sketch of the two main techniques for forming mineral wool. (a) Cascade spinning process; diameter of a spinning wheel: about 160–320 mm. (b) Rotary spinning process (different design for the disk and the fiberizer in the TEL process); diameter of a spinning disk: 300–600 mm.

investigated the relation between shot formation and the initial instability of the melt film on the spinner wheel. The main source of this instability lies in the centrifugal force accelerating the light air toward the denser melt. Finite-element simulations have shown that the size and shape of droplets strongly depend on the size of the initial instability of melt films as described in [3]. The droplet size decreases when the size of the instability is reduced through an increase of the melt temperature. Increasing the rotation speed of the wheel (i.e. increasing the spinning speed) also makes drops smaller, thereby decreasing the shot fraction of the wool product and making at the same time fibers thinner. Furthermore, the shape of melt droplets is influenced by the initial instability domains. In general, it becomes more roundish with increases of melt temperature and surface tension, whereas the droplet front parts get less roundish (or more square shaped) with an increase of the wheel rotation speed. These effects must thus be balanced to optimize both production efficiency and wool performance.

3.2 Rotary Spinning Process

Although stone wools with specially designed compositions can also be fiberized with it, the rotary spinning process is commonly used for the production of glass wool. One of the designs is sketched in Figure 2b. Another is the Saint-Gobain TEL process, which differs regarding the design of both the spinning disk and the fiberizer. In both cases the required high-quality melt is produced in gas-recuperative or oxyfuel furnaces whose capacity ranges from 10 to 200 tons/day for a single line with up to six spinners. As in the cascade process, fibers are spun by a combination of centrifugal force and gas blowing. The former is produced by a spinning disk 300–600 mm in diameter rotating at 2 000–3 000 rpm whose sidewall is perforated with 30 000–50 000 holes ~1 mm in diameter uniformly distributed around the circumference. Disks are made of Fe-, Ni-, or Co-based superalloys (Chapter 5.10), which must not only have outstanding mechanical properties to sustain high rotation stresses at elevated temperatures but also resist glass corrosion and oxidation by the surrounding air. As a matter of fact, such superalloys had to be specially developed for these applications.

When a melt stream falls at a controlled rate into the disk, it is extruded as melt jets through the holes by an outwardly radial centrifugal force. Because melt jets grow and move under the combined effect of viscosity, surface tension, gravity, and aerodynamic forces [5], they are forced into the fiber spinning zone where they are attenuated by a suitable blowing flow. The speed and temperature of the gas flow depend on the design of the fiberizer. There are two different gas flows, which interact with

the arising fiber curtain. One is directed downward at 1500 °C to keep the jets warm and highly deformable near the nozzles. At a temperature of about 30 °C, the other is a highly turbulent cross-stream airflow, which stretches and quenches the hot jets as solid fibers and then pushes them down to a conveyor belt below the spinner. The fibers have a mean diameter of 2–6 μm and a mean length of 2–6 mm. As for the fraction of unfiberized particles, it is lower than 1% because all melt goes through the extrusion stage in the spinning disk.

As evidenced in many experimental studies, the efficiency of the rotary spinning process strongly depends on melt temperature, viscosity, rotational speed of the spinner disk, number and size of the holes in the spinner disk, and the surrounding temperature of the airflows. In general, the process must be conducted at viscosities of 50–200 Pa·s at which melt temperatures range from 950 to 1100 °C. Owing to the complexity of the fiber spinning mechanism, numerical simulations have been conducted to provide insights into the fiber formation. An asymptotic coupling concept was introduced for fluid–fiber interactions [5]. The melt jets cause the airflow to swirl, whereas the fiber jets deflect the burner flow. The resulting axial flow velocity and temperature profiles determine the fiber spinning momentum and the heat exchange, respectively. The temperature of the fiber jets depends on the arrangement of the spinning rows, i.e. on the distance between the burner and the rows of the spinning holes in the disk [5]. Because the jets from the highest rows are warmer than those from the lowest, they have a faster fiber stretching ability and hence yield thinner fibers. But the wool quality requires a narrow diameter distribution of fibers, and therefore nozzle geometry, nozzle diameters, and distances between spinning rows in the disks must be optimized to reduce temperature gradients in the spinning disk. Again, numerical simulations are useful in this respect to model the interactions between the melting and spinning domains and to optimize the process regarding energy consumption and robustness [5].

4 Melt Viscosity and Fiber Spinnability

Spinnability is the ability or suitability of a glass-forming melt to be stretched or spun into defect-free fiber filaments. It first depends on intrinsic factors, of which the most important is the temperature dependence of the melt viscosity (Chapter 4.1). At the same T_g/T (Figure 3), the viscosity is, for instance, lower for stone than for glass wool compositions. This difference has important consequences because higher fiber spinning temperatures are required for the former than for the

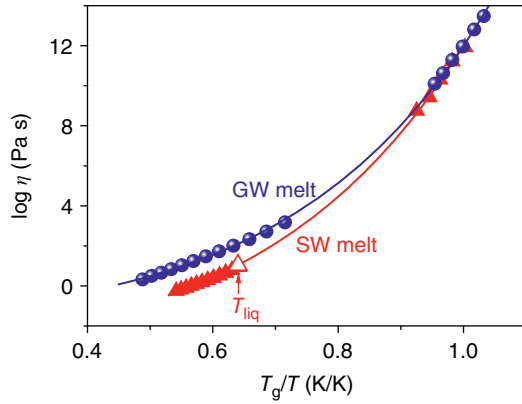


Figure 3 Viscosity–temperature relationships of stone and glass wool melts in a fragility plot where the glass transition temperature (T_g) was measured by differential scanning calorimetry. Liquidus temperature (T_{liq}) also determined by DSC (cf. Figure 4), but not indicated for the glass wool for lack of crystallization signal in DSC thermograms. Solid lines: fits of Eq. (2) to the viscosity data.

Table 2 Composition (wt %) of wool fibers (produced by cascade process) and continuous fibers (produced by bushing process) for studying rheological, thermal, and mechanical properties.

Oxide	Stone wool	Glass wool	Basalt	E-glass
SiO ₂	41.5	66.6	49.3	53.6
Al ₂ O ₃	21.3	0.7	15.6	14.6
TiO ₂	1.6	0.1	1.8	
Fe ₂ O ₃	7.3	0.7	11.7	0.3
CaO	13.9	7.8	10.4	23.5
MgO	11.7	2.3	6.6	
Na ₂ O	1.6	14.1	3.9	0.9
K ₂ O	0.8	0.2	0.7	
B ₂ O ₃		7.0		6.3
P ₂ O ₅	0.3	<0.1		

The wool and continuous fibers with basalt and E-glass compositions were made as model samples [8–10].

latter to obtain similar melt homogeneity, fiber geometry, and wool yields.

For typical stone and glass wool compositions (Table 2), the viscosity is well described by a three-parameter equation [11]:

$$\log \eta = \log \eta_{\infty} + \frac{B}{T} \exp \left(\frac{C}{T} \right), \quad (1)$$

where η_{∞} is the high-temperature limit of viscosity and B and C are constants. Compared with the Vogel–Fulcher–Tammann (VFT) equation, Eq. (1) benefits from a stronger physical foundation that ensures accurate predictions of low-temperature viscosities without any

singularity at finite temperatures [11]. For convenience, it can be expressed in terms of the liquid fragility index (m) and glass transition temperature (T_g) [11]:

$$\log \eta(T) = \log \eta_{\infty} + (12 - \log \eta_{\infty}) \frac{T_g}{T} \exp \left[\left(\frac{m}{12 - \log \eta_{\infty}} - 1 \right) \left(\frac{T_g}{T} - 1 \right) \right], \quad (2)$$

where both m and T_g are obtained from fits of Eq. (2) to the relevant viscosity data. The values of m determined in this way are 46 and 50 for the stone and glass wool compositions, respectively, indicating that the former is more fragile than the latter and thus is slightly less vitrifiable. This conclusion is borne out of the stronger crystallization tendency of stone compared with glass wool compositions as revealed by an intense exothermic peak in a differential scanning calorimetry (DSC) thermogram (Figure 4), which is observed for the former and is lacking for the latter.

Although high glass-forming ability usually translates into high fiber spinnability, the viscosity at the spinning temperature must also be considered because it must be higher than a critical value (η_c) below which too low cohesive forces would prevent the melt from being stretched. Since η_c depends on the structural relaxation time of the melt, it increases with the timescale of the process. For rather slow continuous fiber drawing (via the bushing technique), it should be in the 30–200 Pa·s range, with an empirically favored value of about 100 Pa·s, whereas it may be as low as 1 and 50 Pa·s for the cascade and rotary processes, respectively. In this respect, some flexibility results from the fact that the spinning temperature may be slightly lower than the liquidus as long as crystal nucleation and growth remain relatively slow

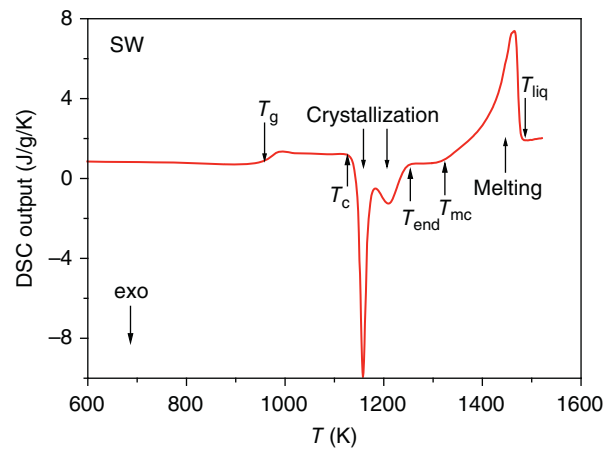


Figure 4 Phase transformations of a stone wool composition as observed in a DSC thermogram for a sample heated under argon at a rate of 20 K/min. T_g : glass transition temperature. T_c and T_{end} : onset and offset temperatures of crystallization. T_{mc} and T_{liq} : onset and offset temperatures of melting.

phenomena (Chapter 5.4). In this case, they do not produce solid inclusions in the flowing melt large enough to hamper the process during the very brief time lapse of spinning.

As a matter of fact, the ratio between the viscosity at the liquidus, η_{liq} , and η_c may be used to characterize the intrinsic fiber spinnability, which is best for the highest values of this parameter as long as specific effects of surface tension can be neglected. This is actually the case for most of the mineral wool fiber-forming melts because differences in surface tension at T_{liq} are much smaller than in viscosity. That η_{liq} is the dominant parameter determining the intrinsic fiber spinnability does not mean, however, that other factors such as surface tension should not be taken into account when designing the fiber spinning process and facilities. And, of course, extrinsic factors must also be considered. As already stated, the spinning speed, centrifugal force, external cooling rate, temperature of the spinning wheel, etc. must all be optimized to obtain an elevated output of high-quality products and achieve enhanced energy efficiency. But further discussion of these engineering factors is beyond the scope of this chapter. A detailed definition and quantification of fiber spinnability are reported in [6].

5 Physical Properties of Stone and Glass Wool

5.1 Thermal and Mechanical Histories

Among glass products, mineral fibers distinguish themselves by the fact that they do not need to be annealed because of a lack of temperature gradient and hence of internal stress resulting from their very small diameters [3]. They are hyperquenched and thus still farther from equilibrium than their bulk counterparts. In addition, the fibers keep a memory of the drawing stresses to which they were subjected during spinning. Hence, the structural atomic disorder and associated potential energy of the fibers reflect the specificities of this thermal and mechanical history with the consequence that the physical properties of these materials differ considerably from those of their bulk counterparts. A simple calculation of the actual cooling rate of mineral wools will illustrate this statement simply.

In a first approximation, the thermal history of a glass can be characterized by its fictive temperature (T_f), i.e. the temperature at which the liquid structure has been frozen in, which may itself slightly depend on the particular property considered. Here, T_f is calculated for the stone and glass wool samples (Figure 5) with an enthalpy-matching approach [12] from the temperature dependence of the isobaric heat capacity (C_p). For this purpose, measurements have been made on heating at 20 K/min

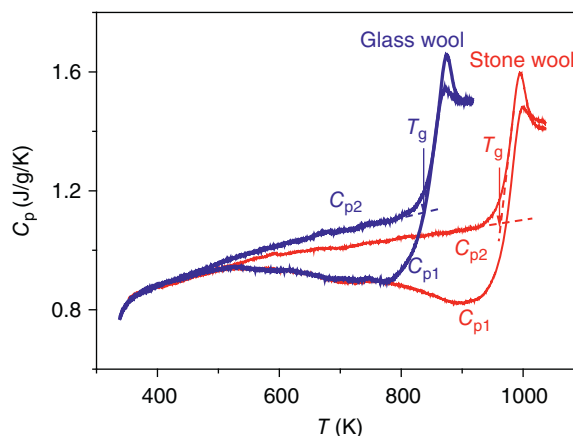


Figure 5 Enthalpy relaxation of stone and glass wool samples determined in DSC measurements of the heat capacity made at a heating rate of 20 K/min through the glass transition range. C_{p1} : measurements on the as-produced sample. C_{p2} : second upscan made right after the first.

first on as-spun fibers (C_{p1} in Figure 5) and then on the same sample cooled down at 20 K/min (C_{p2}), which are in this way annealed as usual. In Figure 5 the areas enclosed by the C_{p1} and C_{p2} curves thus represent the total enthalpy trapped in the fibers by hyperquenching, which are calculated to be 64 and 44 J/g for stone and glass wool, respectively. According to [12], fictive temperatures of 1150 and 975 K are derived from these values for the stone and glass wool samples, respectively, which are 19 and 17 % higher than their standard glass transition temperatures of 960 and 831 K. From the viscosity at T_f , the cooling rate q_c of the fibers can be determined with the relation [12]

$$\log q_c = 11.35 - \log h(T_f). \quad (3)$$

From the viscosity data (Figure 3), one then finds that the cooling rates of the stone and glass wool fibers are distinct at about 10^6 and 10^5 K/s, respectively, even though their parent melts exhibit similar T_f/T_g ratios. The reason for this contrast is that, in fiber spinning windows, the glass wool melt is about ten times more viscous than the stone wool melt at their respective fictive temperatures. In other words, cooling rates must indeed be ten times higher for the cascade spinning process than for the rotatory spinning process to obtain the similar T_f/T_g ratios actually borne out in practice.

5.2 High Temperature Stability

Although fiber crystallization is to be strictly limited during production, this process confers outstanding mechanical properties to mineral wools in fire-protection applications when heated fibers keep upon partial crystallization their shapes up to temperatures of 1300 K or

more. Depending upon the nature of the surrounding atmosphere, the HTS is thus defined as this ability of wool fibers to keep their original geometric shape at high temperatures. For readily vitrifiable glass wools, this ability is virtually nonexistent because crystal nucleation and growth take place at temperatures at which the super-cooled liquid has already sintered as a dense bulk glass that has thus become useless as an insulating material.

As already noted, stone wool fibers in contrast crystallize more readily (Figure 4). Upon dynamic heating at 20 K/min under an argon atmosphere, the augite pyroxene $[(\text{Si,Al})_2\text{O}_6](\text{Ca,Mg,Fe,Ti,Al})_2$ and albite feldspar $[\text{NaAl-Si}_3\text{O}_8]$ precipitate between onset (T_c) and offset (T_{end}) temperatures of about 1125 and 1240 K before melting begins at a temperature T_{mc} of about 1300 K. In this case, however, the HTS is not that high because crystallization does not prevent the fibers from collapsing from about 1100 K.

A higher HTS of about 1350 K is in fact achieved in air thanks to the oxidation of ferrous into ferric iron by an internal redox reaction (Chapter 5.6) whereby Ca^{2+} , Fe^{3+} , and especially Mg^{2+} ions diffuse from the interior toward the surface of the fiber. There, they react with oxygen to form at the fiber surface, mainly periclase $[\text{MgO}]$ as a nanocrystalline layer whose thickness increases linearly with increasing degree of oxidation and can reach about 100 nm for complete oxidation of the ~ 7 wt % FeO content of the material [13]. Although the melt viscosity somewhat increases correlatively upon oxidation, the major effect on the HTS results from the presence of this periclase layer that not only markedly hinders sintering but also allows the softening fibers to keep their shape thanks to the mechanical support they provide. Eventually fiber collapse nonetheless takes place near 1350 K at the onset of melting and of disappearance of the nanocrystalline layer and the interior crystals [13].

5.3 Elastic Modulus and Hardness

The intrinsic elastic and plastic responses of a fiber subjected to an external mechanical load are critical features in any use of insulating wool. They depend on the thermal and mechanical history of the material and, therefore, on the fiber spinning conditions. The relevant parameters in this respect are the reduced elastic modulus (E_r) and hardness (H), which can both be measured with a specifically designed nano-indentation technique [8]. In practice, E_r is defined by the load–depth unloading stiffness S through the relation $E_r = 0.5S\sqrt{\pi/A_C}$, where A_C is the projected contact area at the maximum depth of penetration, S is obtained from the unloading curve slope, and H is defined as P_{max}/A_C , where P_{max} is the maximum load used for indentation. Because these properties also

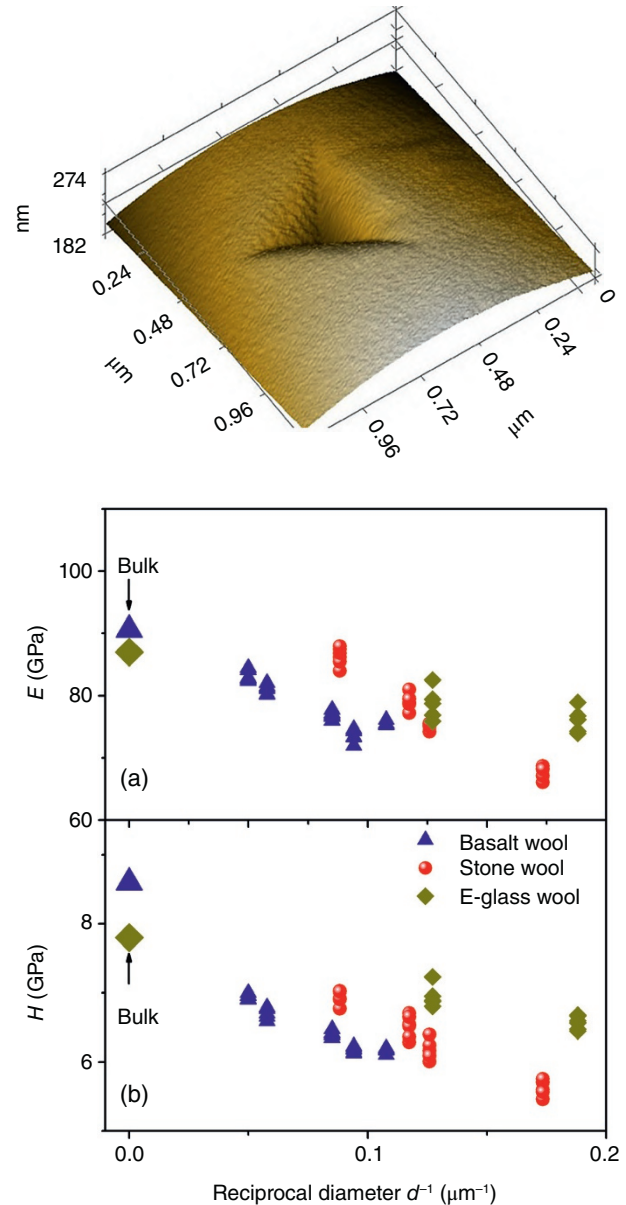


Figure 6 Effect of fiber diameter (as d^{-1}) on mechanical properties of three types of wool fibers as determined with a nano-indentation technique under a load of 1000 μN [8]. (a) Atomic force microscope micrograph of an indent on the surface of the stone wool fiber with a diameter of about 6 μm . (b) Reduced elastic modulus (E_r). (c) Hardness (H).

vary with chemical composition, we summarize in Table 2 the results obtained for stone, basalt, and E-glass wools, the last one – also prepared with the cascade spinning process – serving as a reference for the two others.

Actually, the most important parameter to be investigated is the fiber diameter d , which itself increases with decreasing cooling rate and fictive temperature. When plotting E_r and H against the reciprocal of d , so as to include bulk glass properties, one observes that both increase with it (Figure 6). The reason is of course that

glasses with a higher T_f have more open structures and, hence, a lower resistance to elastic and plastic deformation and densification. Interestingly, these variations for a given glass are larger than the differences between the three glasses for a given diameter, E-glass having the highest moduli (as expected from its use in reinforcement; cf. Chapter 1.5).

5.4 Tensile Strength

Even though much work has been done on fiber fracture, the process is not well enough understood yet because it depends on a combination of factors such as chemical composition, melt homogeneity, thermal and mechanical histories, fiber shape and size, and surrounding atmosphere. Here we will limit ourselves to the relationship between the tensile strength and the axial stress exerted upon fiber drawing for the basalt sample of Table 2, taking again as a reference E-glass continuous fibers spun through the nozzle of a 90Pt/10Rh (wt %) crucible. For all samples the tensile strength was measured at room temperature for a relative humidity of 80% [9]. For both glasses, the tensile strength first increases very strongly up to a σ_{ax} of about 10 MPa and then reaches a plateau at about 3100 MPa for E-glass (Figure 7a) and ~3500 MPa for basalt (Figure 7b). Since wool fibers are stretched at a lower axial stress (caused by centrifugal force) than continuous fibers, but at a higher stress than the bulk glass, the fiber drawing force appears to be a key factor to determine the fiber strength.

Because the structural anisotropy of the fibers linearly increases with σ_{ax} [10], the orientation of structural units along the fiber axis initially plays a positive role in enhancing tensile strength. Upon fiber spinning, the defects also become stretched and oriented along the fiber axis at much smaller shear stress or axial stretching than structural units. Like oriented species or structural units present in other materials, they should then reduce the probability of catastrophic fracture. However, the existence of a plateau above a certain σ_{ax} suggests that other factors then come into play and start to cancel out the

positive effect of the structural orientation on the fiber strength. Defects such as microbubbles, seeds, striae, and structural heterogeneities are inevitably present and represent potential sources of fracture (Chapter 3.11). In other words, the tensile strength of fibers will no longer be enhanced just by increases of the structural anisotropy.

Of particular interest is finally the large excess of tensile strength of the wool fibers (1500 MPa) over the bulk glass (80–200 MPa) indicated as Interval 2 in Figure 7. This excess likely originates in two major effects: (i) a lower probability for the presence of surface flaws on fibers compared with bulk glasses and (ii) the lack of oriented features in bulk glasses.

6 Biopersistence and Biodurability

Owing to the morphological similarity between mineral wool and asbestos, much work has been done to determine whether mineral wool could be cleared by the lung physiological mechanisms, through dissolutions, breakage, phagocytosis and mechanical removal via the mucociliary escalator. Experimentally *biopersistence* is investigated *in vivo*, whereas *biodurability* or dissolution rates refer to *in vitro* measures of dissolution [14, 15], which reflect the chemical degradation (dissolution) of the fibers but not the physical clearance.

As a first step, specific *in vitro* tests have been performed to determine the dissolution rate of the mineral wool fibers as a function of chemical composition in an environment mimicking that of the lung. Appropriate conditions are met with a medium similar either to the near-neutral (pH 7.4) extracellular lung fluid or to the acidic (pH 4.5) regime defined by the phagolysosomes of the macrophages present in the lung. In addition to being dissolved, the fibers can also be removed mechanically from the lung via macrophage clearance.

An important feature is that dissolution in the lung is more rapid for mineral wool than for crystalline fibers because the former, with its long-range disordered

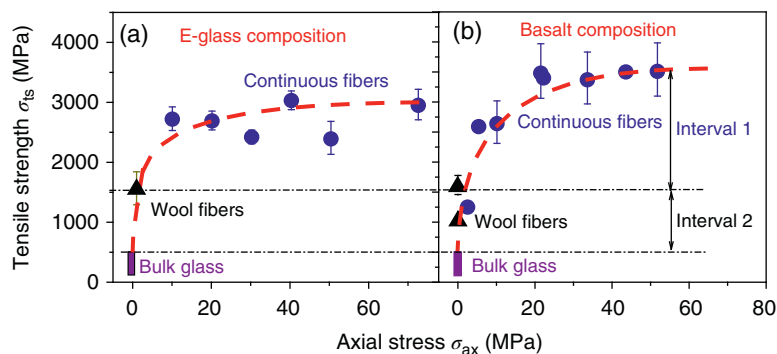


Figure 7 Increases of tensile strength σ_{ts} with the axial drawing stress of fibers (σ_{ax}) (replotted from [9]). (a) E-glass fibers. (b) Basalt fibers. Interval 1: σ_{ts} difference between continuous and wool fibers for similar diameters. Interval 2: σ_{ts} difference between wool fibers and bulk glass of the same compositions.

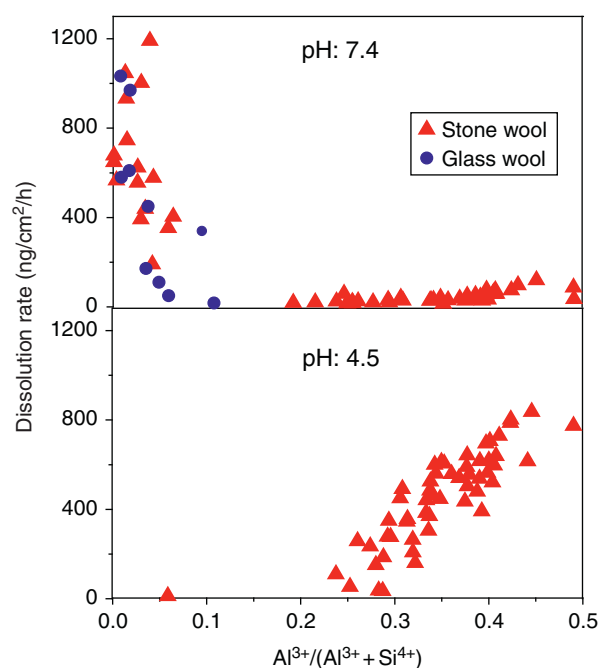


Figure 8 Effect of pH and chemical composition on the dissolution rate of glass and stone wool fibers. Source: replotted from [18].

structure, is metastable relative to the latter and thus has a larger thermodynamic driving force (i.e. larger decrease in Gibbs free energy) for dissolution. As the dissolution rate depends on glass composition, numerous *in vitro* studies have been carried out with the dual purpose of predicting this dependence in terms of the different structural units of the glass network and the simulated lung fluid and of correlating the results with *in vivo* biosolubility. For high-alumina low-silica glasses (i.e. with >7 wt % Al_2O_3 and <43 wt % SiO_2), the *in vitro* dissolution rate at pH 4.5 correlates with the *in vivo* biosolubility [16], whereas for low-alumina glasses (i.e. with <5 wt % Al_2O_3), the *in vitro* dissolution rate at pH 7.4 correlates with the *in vivo* biosolubility [17]. Thus, the dissolution rate indeed reflects *in vivo* biosolubility.

In most cases, a mineral wool fiber composition with a higher dissolution rate at pH 7.4 shows a lower dissolution rate at pH 4.5 and vice versa [18]. Alumina has indeed a strong but complex effect on the *in vitro* dissolution rate (Figure 8). At pH 7.4, the dissolution rates of both stone and glass wool fibers drastically decrease with increasing alumina content up to ~5 wt %, i.e. up to a $Al^{3+}/(Al^{3+} + Si^{4+})$ ratio of ~0.07 (Figure 8a). Above 5 wt % alumina, the dissolution rate only slightly increases. In contrast, at pH 4.5 (Figure 8b), the dissolution rate of stone wool fibers remains almost unchanged with $Al^{3+}/(Al^{3+} + Si^{4+})$ ratio up to about 0.25, and then increases linearly. Based on these findings, low-biopersistent stone wool fibers have been developed along two different

routes. One is to adjust the alumina content to a level above 14–16 wt % and the silica content to below 42–43 wt %, whereas the other is to lower the alumina content to below 3–4 wt %. Both types of fibers have demonstrated high biosolubility according to *in vivo* tests. In addition, the absence of relevant pathogenicity and a lack of anomalous neoplastic changes have been observed in long-term inhalation tests on these fibers.

7 Perspectives

In today's complex markets, a single insulating material cannot satisfy all possible requirements. Silica aerogels have, for instance, record low thermal conductivities, but their high cost restricts them to niche applications (Chapter 8.3). Polyurethane foams are the main other products having a lower thermal conductivity [of about 0.028 W/(m·K)] than mineral wool, with the advantage of good mechanical properties but the disadvantage of flammability. Although improvements in physical performances and development of new compositions with low biopersistence have been made in the past two decades, a potential remains to develop even better products along with more efficient fiber spinning processes. A better understanding of the relations among chemical composition, fictive temperature, viscosity, and cooling rate is, for instance, critical for optimizing both cascade and rotary fiber spinning processes with respect to fiber output and quality. Likewise, a physically based value for the highest fiber spinning efficiency still needs to be found through numerical modeling and molecular dynamics simulations in combination with experimental studies.

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9.4

Glasses for Solar-energy Technologies

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1 Introduction

According to the International Energy Agency (IEA), the worldwide energy consumption was 574×10^{18} J in 2014, of which only 0.24% was solar in origin in the form of electricity or heat. By comparison, sunlight brings about 4×10^{24} J/yr to the Earth (annual solar energy = average sun irradiance at ground level [1050 W/m^2] times the Earth's surface exposed to the sun [$(4/\pi) \times 10^{14} \text{ m}^2$] times seconds in a year [3.1×10^7]). Even if one considers that the ocean and other uninhabitable areas represents 90% of the Earth's surface, the energy directly harnessed from sunlight represents less than 10 ppm of the amount received in inhabited areas. The motivation for increasing significantly this fraction is thus clear, especially as one may in addition expect an improved energy security, less pollution, a lesser human footprint, or even more stable prices for fossil resources.

In this respect, the basic point is that all types of solar conversion systems rely on glass, to such an extent that for some them this material is simply without any alternative [1, 2]. The combination of transparency, chemical inertness, strength, rigidity, and high-temperature stability is in effect unique to glass. Additional advantages are almost limitless shapability, which makes production of versatile geometries such as tubes and panes at large scale possible, as well as surface tailoring by physical or chemical means. Besides, glass is an environmentally friendly material as it is not only free of carcinogenic, mutagenic, and reprotoxic substances but also 100% recyclable (Chapter 9.9). Sustainability over its entire life cycle thus manifests itself in a cradle-to-cradle certification of most glass products for solar applications.

After a sketchy review of the energy problem, this chapter will thus describe the various uses of glass in the variety of solar-energy devices currently in use or still under study. Photovoltaic (PV) cells will be first considered, followed by solar heating devices, solar thermal-power plants, natural and artificial photosynthesis processes, chemical water splitting, and finally desalination and disinfection setups.

2 The Energy Problem

The International Energy Outlook 2016 released by the U.S. Energy Information Administration forecasts that the worldwide marketed energy consumption will rise by 39% between 2016 and 2040. The strongest growth is expected for countries not belonging to the Organisation for Economic Co-operation and Development (OECD), particularly in Asia. Fossil fuels (oil, coal, and natural gas) have the largest share (82%) on the world's energy consumption today and are predicted to account for 78% of global energy used in 2040. Ever since the Industrial revolution, the atmospheric concentration of carbon dioxide has increased steadily at an annual rate of about 0.5% in 2015 (see, for instance, the observations begun in 1958 at the Mauna Loa Observatory in Hawaii known as the *Keeling curve*, released daily by the Scripps Institution of Oceanography at UC San Diego). Because 90% of human CO₂ emissions result from the combustion of fossil fuels for electricity, heat, and transport, future energy use has emerged at the center of the current climate debate. Deep cuts in CO₂ production have in particular been called in countries such as China and the United States, which are by far the biggest world emitters.

Besides a general reduction of energy consumption, the supply of primary energy from carbon-neutral sources has become one of the society's most important

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challenges. Hence, most industrialized countries have established fiscal incentives and legal instruments such as the pioneering *Renewable Energy Sources Act* in Germany to decrease the initial market entry barriers of solar-energy systems and to reduce the costs for production and consumption over a period of time.

Glass contributes to the primary energy demand to produce materials incorporated in solar energy conversion devices and to a lesser extent of about 13% for single-crystal and thin-film PV modules, respectively. Because the payback times for today's solar technology systems are substantially shorter than their expected lifetimes, increasing the use of glass in such devices remains relevant in terms of sustainability and carbon footprint. With an energy expense of 2500–2800 kWh, about 450–500 kg of CO₂ are emitted when 1000 kg of glass are melted to make about 130 m² of 3 mm-thick glass panes, not counting the other 160–180 kg resulting from the decomposition of soda ash, limestone, or dolomite (Chapter 1.3).

3 Solar Electricity

3.1 First- and Second-generation Cells

PV cells are designed to convert directly solar energy into electricity. Two generations of cells are currently produced (Figure 1). The first is still having a very large market share of 90% in 2015 with wafers made up of either single-crystal (sc-Si) or polycrystalline (pc-Si) silicon [3–5]. Most such modules have a single sheet of glass as front material and a non-glass back cover. Glass is also found in electrode materials to ensure efficient contact with the silicon. For building integrated concepts, square cells are laminated between two glass plates.

The second generation PV cells rely on thin-film technologies based on cadmium telluride (CdTe), copper indium (gallium) diselenide (CIS/CIGS), and amorphous and microcrystalline silicon (a-Si/ μ -Si) semiconductors. In this case one builds the cell by depositing transparent

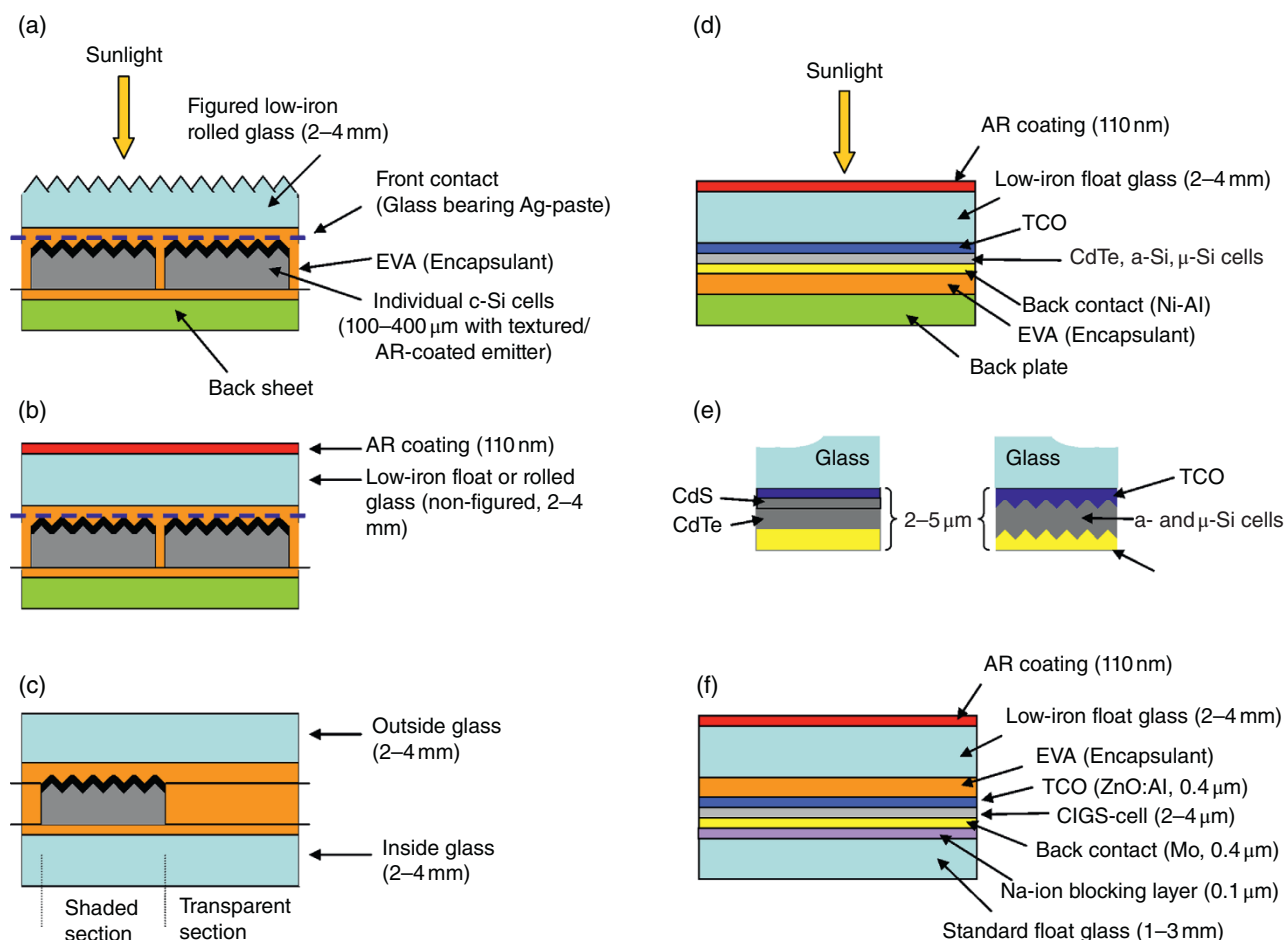


Figure 1 Low-iron glasses in photovoltaic cells. Left: first-generation Si modules with a figured rolled glass cover (a), an AR-coated float glass cover (b), or two float glass panes for building integration (c). Right: second-generation thin-film modules, with AR-coated float glass as a generic superstrate (d), textured and non-textured TCO and back-contact layers (e), and float glass coated with an Na-blocking layer serving as a substrate for CIGS cells covered by a second float glass pane with an AR-coating (f).

electrodes and semiconductor layers onto a sheet of glass in two different configurations, namely *superstrate* (sunlight illumination through this glass sheet) or *substrate* (a nontransparent material can also be used as substrate). A back glass sheet is laminated to the superstrate to encapsulate the device or a non-glass back cover is used. For substrate configurations, a glass plate is laminated as front cover.

3.2 Front and Back Glasses for PV Modules

The front glass ensures the mechanical robustness of the entire PV module, hermetically protects the cell from the environment, and maintains the high transparency of the semiconductor layer. The front is usually made of soda-lime-silicate glass whose relatively high coefficient of thermal expansion (CTE) of 8–9 ppm/K is not problematic in view of the lack of important thermal stresses experienced. The glass is thus made with either the float or rolled-plate process (Chapter 1.4) with a thickness that is commonly 3.2 mm but can range from 2 to 4 mm depending on the module type. The front glass contributes to two third of the module weight (crystalline silicon) but this fraction can increase to more than 90% for thin-film cells with both glassy front and back.

Rolled-plate glass has a structured surface that makes lamination easier, provides a non-blinding effect (no hazard to air navigation), and nicer aesthetics. Plates can also be figured if the rolls carry a pattern. A high-relief pattern such as diamonds is then impressed in the soft glass to increase light trapping, whereas a burred surface structure is often used to enhance the adhesive strength between the glass plate and the encapsulant material, which is most commonly ethyl vinyl acetate $[(C_4H_6O_2-C_2H_4)_n]$ (Chapter 8.8). This material provides mechanical support, optical coupling, electrical isolation, and environmental protection of the PV cell. With currently more than 80% of the market share, rolled-plate glass is increasingly used for both sc- and pc-Si cells.

For second-generation thin-film cells, the float industry offers various types of coated glasses meeting the specific requirements of the different modules, thanks to the extremely plane and smooth surfaces obtained on both sides (root-mean-squared roughness $R_a < 0.5$ nm). For CIS/CIGS cells, a SiO_2 passivation layer is applied directly on the glass surface to prevent migration of sodium from the glass into the cell structure before coating with transparent conductive oxides (TCO), whereas molybdenum is first coated on the back glass. For a-Si/ μ -Si cells, the TCO material itself is deposited in a textured form to trap photons by internal reflection in both TCO conductivity (sheet resistance) and light trapping (haze).

Both float and rolled front glasses are thermally strengthened by airflow quenching after heating at about

620–650 °C (Chapter 3.12) to improve glass strength by a factor of about 4, with a flexural strength in the range 120–200 MPa depending on thickness, edgework, etc. Front glasses are also coated with a broad-band antireflective (AR) layer to minimize reflective losses at the surface of the solar module. Although different types of reflection-controlling layers are commercialized, a single coat of a sol-gel-derived nanoporous silica (Chapter 8.2) has become the golden standard with more than 90% market shares, thanks to its cost efficiency, mechanical stability, and bandwidth.

The coating relies on the formation of an effective optical material of low refractive index. According to Fresnel's law, under normal incidence the refractive index of the AR-coating should be the root square of that the front glass, i.e. $n_{\text{coating}} = 1.23$ for a soda-lime-silicate glass ($n_{\text{glass}} = 1.52$). Depending on the mixing model selected (Lorentz–Lorenz or Drude), a porosity of 47–55% is needed to achieve such a low refractive index from coexisting silica ($n_{\text{glass}} = 1.46$) and air ($n = 1$). Deposits are made a quarter-lambda thick to ensure the optimum in the destructive interference between the sunlight reflected at the air/AR-coating surface and AR-coating/glass interface, that is $\lambda/4n_{\text{coating}} \approx 110$ nm for the peak intensity wavelength ($\lambda = 500$ nm) of the solar radiation.

In the majority of processes, the final porosity and adherence with the front glass is achieved during the heat treatment made for thermal strengthening. Sodium migration from the bulk glass into the AR-coated interface is then beneficial to ensure the high mechanical stability of the coating. One can make the deposition by rolling or spraying an aqueous dispersion of silica colloids on one side of the front glass plates or by dipping the glass sheet into the coating solution and withdrawing it with a constant speed [6]. An alternative is spraying of an aqueous potassium-silicate solution, which then dries into a gel of interconnected silica colloids and dispersed potassium hydroxides and carbonates [7]. To achieve nanopores between silica particles, the latter materials have to be washed away in a subsequent cleaning step. In addition, subwavelength periodic or stochastic surface-relief structures are designed to reduce efficiently reflective losses [8]. An AR-coating can consist of a larger fraction of open porosity that leads to capillary condensation and stronger surface alteration under long-term environmental exposure. The degree of open porosity depends on the type of silica colloids (hollow versus dense particles) and their connectivity (grading) after thermal consolidation.

The use of low-iron content glass is intended to reduce the absorption of sunlight by the front glass sheet itself [9]. Soda-lime-silicate glasses are thus made from high-grade sand, which cuts the total iron content to below 0.014 wt % Fe_2O_3 (=100 ppm w/w Fe). Ferric iron absorbs sunlight from the ultraviolet (UV) region by the low-

frequency tail of a strong charge-transfer band around 220 nm and by intramolecular d–d electron transitions at 385, 420, and 435 nm (molar extinction coefficient up to 4.8 l/mol/cm), whereas ferrous iron has a broad absorption band centered around 1060 nm in the near infrared (NIR) part of the solar spectrum (molar extinction coefficient 54 l/mol/cm) (Figure 2, see also Chapter 6.2). As a result of reducing conditions created by sulfur fining and carbon additions, the absorption bands of Fe^{2+} are usually the most intense. Oxidizing agents like cerium oxide are thus added to the batch to increase its $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, others (e.g. antimony oxide) being avoided for environmental reasons. But a negative side effect then is the formation of photoinduced electron and positive hole centers upon prolonged and intense sunlight, which causes glass discoloration by shifting the UV edge into the visible frequency range. To overcome this *solarisation* problem and, thus, make radiation-stable glasses, a mix of different oxides for the redox control of polyvalent iron is used in practice.

The achievable transmittance τ of the front glass in the PV-relevant range of wavelengths can be derived from conservation of energy as $\tau = 1 - (\alpha + \rho)$ where α and ρ

are losses due to absorption and reflection of light in the volume and at the surfaces of the glass sheet, respectively. According to Beer–Lambert law, the attenuation of light depends on both the concentration of the absorbing species and thickness of the glass plate. Thus, a thinner front glass plate reduces not only the weight of the module but decreases also absorption losses. In the range 300–1100 nm the peak transmittance of a 4 mm-thick low-iron float glass at normal incidence is 91.3% (Figure 2). The reduction of the thickness to 3 mm results in a gain of about 0.2%. A figured low-iron rolled glass can reach a slightly higher value but shows a stronger gain if larger angles of incidence are considered. Another gain of peak transmittance of about 4% on both floated and rolled glass is obtained with a single-side AR-coated low-iron solar glass.

N.B. In photovoltaics, normalization of the transmittance is usually done in terms of the photon flux of the sun, which is the number of photons per area per time ($\text{m}^{-2} \text{s}^{-1}$). To convert the energy flux of the reference spectra (AM1.5g) in a photon flux, the spectral irradiance thus has to be divided by the photon energy $= hc/\lambda$ (h = Planck constant, c = speed of light). With a photon

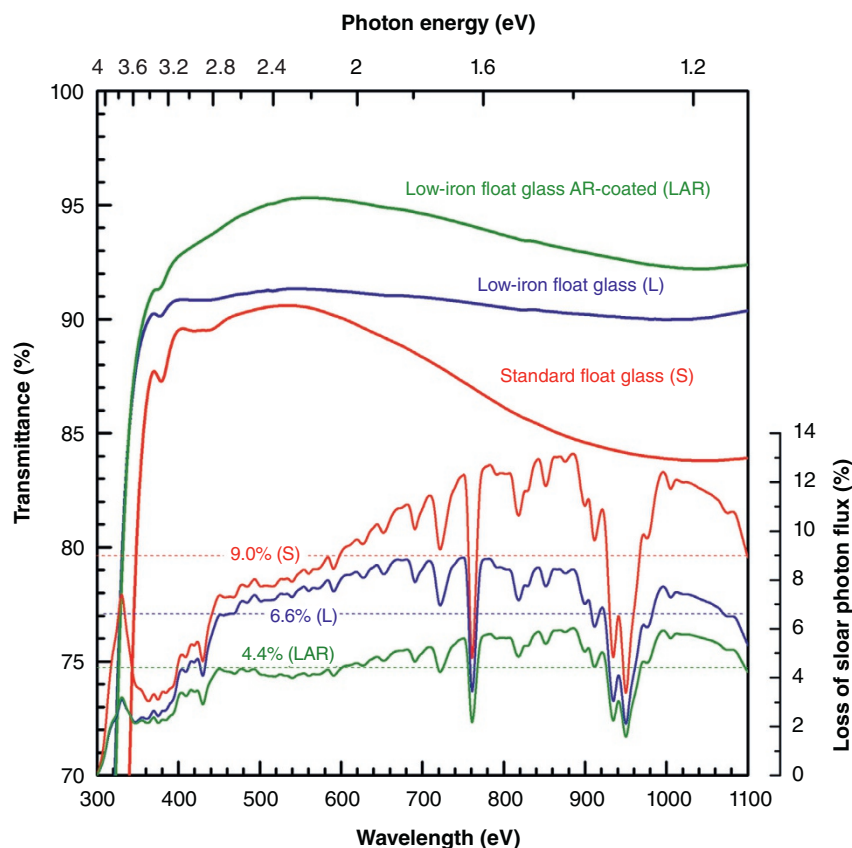


Figure 2 Spectral transmittance and loss of photon flux of different float glass qualities (4 mm thickness) for covering c-Si photovoltaic cells. Average loss of solar photon flux (300–1100 nm) indicated by dashed lines.

flux loss $(\alpha_p + \rho_p) = 4.4\%$ and a band gap of c-Si at 1.12 eV ≈ 1100 nm, a state-of-the-art single AR-coated low-iron float glass can then transmit more than 95% of the PV-relevant number of photons (Figure 2).

3.3 Double-sided Glass Modules for Building-integrated Photovoltaics

When laminated between two glass panes, PV cells can be integrated in the envelope of a building in the form of balustrades, sunshades, facades, or canopies. The energy balance of the building can thus be improved not only by the conversion of solar energy into electricity but also by the shading function that reduces direct energy transmission through the modules. Since PV cells of the first generation are opaque, changing the distance between them (spacing) allows one to adjust the total light transmission and electricity output of the glazing. In *building-integrated photovoltaics* (BIPV), glazing is commercially produced from thermally strengthened glass panes with an external AR coating. Besides crystalline silicon cells which form larger strings with spacing between the cells, also thin-film a-Si PV cells are used for BIPV. For the latter concept, the cell surface covers practically the total surface of the glazing but allows some light to pass through so that the transmission is about 20%.

3.4 Glass-bearing Front Electrode Materials

Finally, glass is also an important but hidden component to contact both sc- and pc-Si cells to the front side. For this purpose, pastes containing a silver powder and up to 10 wt % of a BaO-, Bi₂O₃-, and ZnO-containing borosilicate glass of low softening temperature dispersed in an organic binder are commonly used. They are deposited via screen printing or other techniques and fired quickly in an infrared belt kiln. Upon firing, the glass initially softens and then dissolves at higher temperatures the metal into its structure in the form of Ag⁺ ions. On the wafer side, the glass etches the thin, AR oxide layer of the wafer, whereas Ag⁺ ions are reduced to Ag⁰ to form a direct contact between silicon and the highly conductive silver metal.

4 Solar Heat

4.1 Irradiance and Working Temperatures

In this type of conversion systems the relevant parameter is the solar energy flux, or irradiance, which is simply the power received per unit area (W/m²). The solar radiation absorbed is primarily used to heat up a transfer medium (liquid or gas). In secondary processes, the heat is

exchanged with another liquid (water heating), stored (molten salts), transformed into mechanical energy, and finally into electric power (steam engine).

Reflectors can be integrated to increase the irradiance by redirection of the sunlight to the receiver. This irradiance ($\dot{Q}_{\text{solar}}$) is then the product of terrestrial insolation, that is the solar power at the latitude of interest (e.g. 1000 W/m for Europe and North America), the collector efficiency, the geometric ratio of the reflector-to-receiver area or solar concentration factor (C), and the unit area per reflector. In case of concentrated solar power systems, C exceeds unity and the temperature of the receiver (T_R) increases with it. In such a chain, the total energy conversion efficiency is the product of those of the individual conversion steps [10].

For the first conversion of solar radiation into heat, the efficiency of the receiver (η_R) is given by $\eta_R = (\dot{Q}_{\text{abs}} - \dot{Q}_{\text{lost}}) / \dot{Q}_{\text{solar}}$, where the absorbed heat $\dot{Q}_{\text{abs}}$ is $\dot{Q}_{\text{solar}}$ times the absorption coefficient of the receiver material, whereas $\dot{Q}_{\text{lost}}$ is governed by the radiative and convective heat losses of the hot receiver. The former loss is proportional to the area of the receiver and the emissivity of the receiver's surface and increases as the fourth power of the receiver temperature according to Stefan-Boltzmann law. For a solar power plant, the second energy conversion is heat-into-mechanical work for which the efficiency is that of a Carnot engine $\eta_{\text{Carnot}} = 1 - T_{\text{cold}}/T_R$ operating between the hot thermal reservoir, that is T_R and the cold thermal reservoir (T_{cold}). Thus, two temperature effects oppose each other as the efficiency of the Carnot cycle increases when T_R increases whereas that of the receiver decreases.

For a given solar irradiance or concentration factor, the optimum receiver temperature is, therefore, lower than the maximum value. It can be determined from the first derivative of the total efficiency with respect to T_R . In this way one finds that the optimum operating temperature of a trough receiver is about 400 °C for oil-based heat-transfer fluids, 550 °C for molten salts or direct steam (C up to 100), and about 1000 °C for tower receivers with $C > 1000$. Whereas (alumino-)borosilicate glass with a CTE of 3–4 ppm/K can be used in the former systems, silica glass with its CTE of 0.5 ppm/K must be selected in the latter (Figure 3). These temperatures have thus important implications for the materials to be used for making the receiving units.

4.2 Rooftop Water Heaters

Currently two types of water-heating systems with rooftop receivers are sharing major market segments in the residential and commercial sectors. These systems differ by the fact that they have in-house heat exchangers and

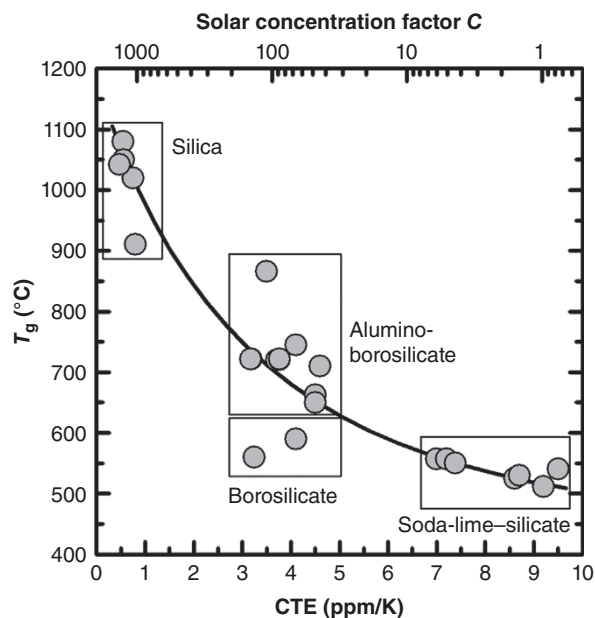


Figure 3 Glass transition temperature T_g of glasses used in solar-energy conversion systems as a function of the coefficient of thermal expansion CTE and the factor of solar concentration C .

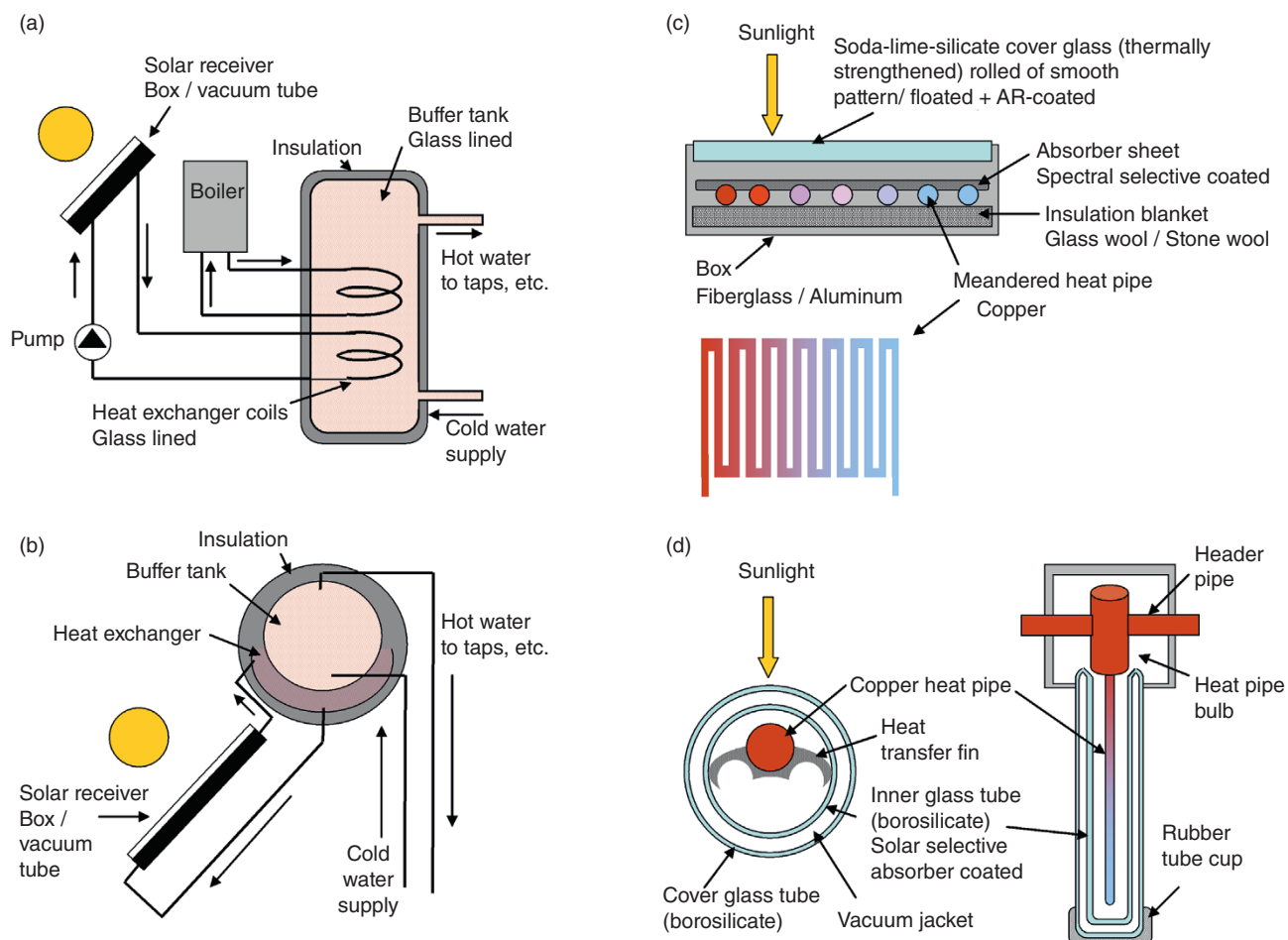


Figure 4 Solar water heaters. Left: rooftop receiver with in-house boiler and heat exchanger for temperate areas (a), rooftop receiver with rooftop heat exchanger for tropical and subtropical regions (b). Right: box receiver (c), evacuated tube receiver (d).

boilers in temperate areas (Figure 4a) and also rooftop exchangers in tropical and subtropical regions (Figure 4b). In both cases glasses are used as cover panes or evacuated tubes in the receiver and as lining in the drinking water-buffer tanks of the heat exchanger.

A box receiver for water heating comprises an insulation layer made up of stone or glass wool (Chapter 9.3), the actual absorber sheet (metal) with a fused meandered pipe loop (copper) and a cover glass pane that seals the metal housing for protection against the surroundings (Figure 4c). To minimize the emissivity ε of the absorber sheet, coatings with a high wavelength selectivity (>15) are used. The wavelength selectivity is the ratio of the absorbed solar radiation between 0.3 and 4 μm to the emitted IR radiation between 4 and 40 μm , where the IR emission is defined as unity minus the IR reflectivity. As a cover, a low-iron soda-lime-silicate pane is used, either an AR-coated float glass or a rolled glass of smooth pattern, which is usually strengthened thermally to increase its mechanical performance.

An evacuated tube receiver unit consists of parallel glass tubes set in a metal frame or – in some products

– of glass tubes placed on top of a parabolic Al-mirror sheet. Each glass tube is double-walled, one-side-closed and evacuated to suppress conductive heat loss (Figure 4d). To reduce also radiative heat loss, the inner surface of the inner wall has a low-emissivity coating typically made of an AlN/AlN-SS/Cu triple layer ensuring $\epsilon < 8\%$ at 80°C . The solar energy transmittance τ_e of the outer borosilicate glass wall should exceed 90% in the 300–2500 nm wavelength range (Figure 5).

A copper heat pipe is centered within the tube, comprising a long hollow pipe with a large-diameter bulb at the top-end. In some other tube receivers, the heat pipe is positioned directly against the inner glass wall on the sun-exposed side, whereas the welded-aluminum heat-transfer fins are curved to track the sunlight throughout the day. Within the closed heat pipe, water is under a pressure lower than 50 hPa to evaporate at around 30°C . The vapor rises to the bulb at the top-end (i.e. outside the glass tube), where its heat is exchanged. Upon condensation of the cold vapor, water runs down to the hot-end of the heat pipe inside the glass receiver, and so on. The evacuated tube ($<1\text{ mPa}$) is usually made from borosilicate glass (Chapter 7.6) with a 50–70 mm diameter and a distance of about 5 mm between the inner and outer walls. The thickness of the walls is 1.6 mm (inner) and 1.8–2.0 mm (outer) and the length is up to 2 m.

The inner surfaces of the drinking-water buffer tank and the solar-heating coils within it are frequently glass-lined. This enameling serves to increase the durability with respect to hot water and to comply with drinking-

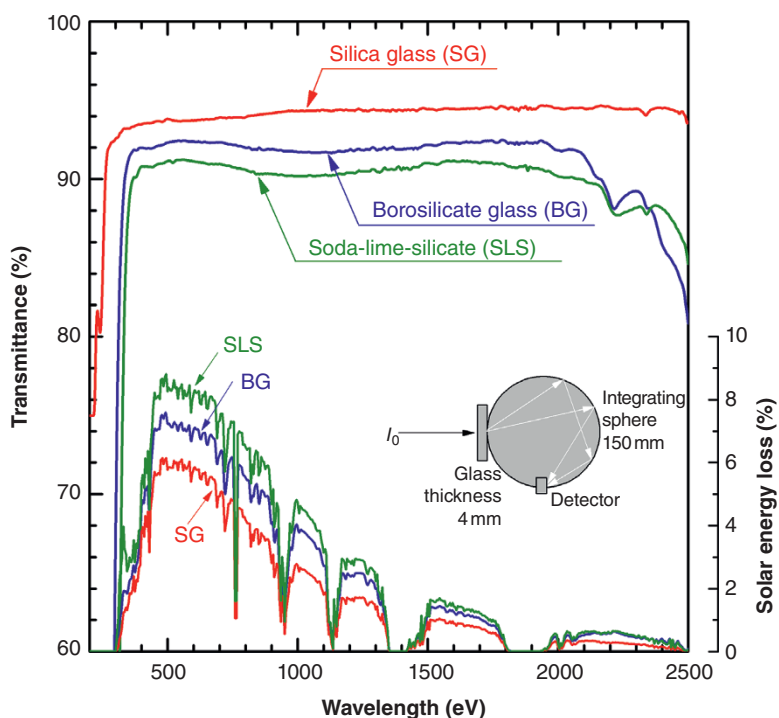
water regulations in terms of metal-ion migration. Standard enameling is performed by a two-coat, two-fire technique with a total thickness of about $300\text{ }\mu\text{m}$. Enamels are typically multicomponent glasses of a borosilicate base with suitable CTE and T_g values for the coated steel. Specifically, the enamel must be kept under compressive stresses, which implies that the CTE of the ground-coat enamel is about 3 ppm/K lower than that of the steel, whereas that of the cover-coat enamel is another 0.5–1.5 ppm/K lower. It happens that top-coat enamels of low CTE are rich in network formers, which ensures the desired hydrolytic resistance.

4.3 Solar Thermal-power Plants

Glasses are used in both collector and receiver units of solar thermal-power plants. In most applications a back-side silvered glass mirror collects the solar radiation. For these mirrors, glass is a protective barrier, a light transmitter, and, in part, a structural support, whereas glass tubes (trough) and windows (tower) are integrated in receivers mainly to suppress convective and conductive losses.

For trough receivers, mirrors are bent in a parabolic shape. The solar irradiance is reflected onto the evacuated tube receiver which is positioned on the focus line while the collector tracks the sun from east to west during the day. In tower-power plants, plane glass mirrors (heliostats) are used as rotating reflectors to keep reflecting

Figure 5 Spectral transmittance and solar-energy loss of 4 mm-thick low-iron soda-lime-silicate, borosilicate, and silica glasses used for solar-thermal applications.



sunlight toward the receiver positioned on the top of the tower.

Bent and plane mirrors are made of tempered low-iron soda-lime-silicate float panes of a 2–4 mm thickness with an edge finish for safe handling and mechanical robustness. For parabolic mirrors the plane glass is sag-bent before being strengthened (Chapter 9.2). The glass is then coated in the superstrate configuration. Whether plane or parabolically curved, all mirrors are silvered (usually wet chemically) and the back of the delicate Ag-layer is protected by a copper layer and then by paint layers to assure the high durability of the reflective coating. Along with a solar-energy reflectivity (ρ_e) higher than 94%, the precision of curvature to better than 2.0 mrad and the mechanical shape stability of the parabolic mirrors are key parameters for the reflector efficiency in trough applications. This is particularly evident for the large reflector apertures and smaller diameters of absorber tubes that are required for high-temperature transport fluids such as molten salts ($T_R = 550^\circ\text{C}$).

A tube receiver comprises an evacuated outer glass tube at a residual pressure lower than 0.1 Pa and an inner metal-pipe loop with a low-emissivity coating ($\epsilon < 10\%$ at 400°C). The outer tube is made of AR-coated borosilicate glass of solar energy transmittance τ_e higher than 97% between 300 and 2500 nm. It is commonly of 120–125 mm outer diameter (2–3 mm wall thickness), up to 4 m long, and sealed with fused metal bellows at both ends to account for the higher thermal expansion of the inner absorber pipe. For power plants operating with oil-based heat-transfer fluids (T_R up to 400°C), glass tubes are equipped with getter materials and a noble-gas capsule. The former captures the hydrogen produced by the decomposition of the thermo oil, which permeates through the metal pipe into the vacuum of the glass envelope, whereas the latter injects noble gas at the end of the getter capacity into the glass tube to maintain a low conductive heat loss over an extended operating period.

Tower-power plants can comprise a silica-glass window that encloses the aperture of the receiver and separates two pressure or temperature zones. For pressurized air receivers, the window is dome shaped, whereas for unpressurized volumetric receivers, one must assemble segments of silica-glass tubes as imposed by manufacturing constraints for aperture exceeding 1 m^2 . In both cases, the window is AR-coated to suppress reflective loss [11], whereas temperatures are kept lower than 1000°C by active cooling to reduce inter alia the formation of defects, such as those from surface contaminations that could not be cleaned up [12].

Concentrated solar energy can also be used for steam generation in oilfield operations. Enclosed trough receivers have been developed to protect the reflector and receiver surfaces from windborne sand, dust, humidity,

and other harsh conditions often prevailing in the environment of oilfields [13]. In these steam plants the entire reflector-receiver units are sheltered in agricultural greenhouses. The curved back-side silvered glass mirrors are then replaced under the sealed glass-skinned structure by a lightweight aluminum honeycomb construction. Soda-lime-silica float glass is used for the glazing of the greenhouses, which is kept clean with automated washing machines.

5 Solar Fuels

5.1 Natural and Artificial Water Splitting

A fuel can be defined as a simple chemical reductant, easy to transport and store, which reacts (“burns”) on demand with the oxygen of the air and releases much energy [14]. In contrast to fossil fuels (oil, gas, and coal), which originated in ancient photosynthesis and are stored in geologic deposits, solar fuels are generated by natural and artificial photosynthesis either directly or by fermentation upon short lifetime cycles. The basic process is the direct conversion of solar energy into chemical energy. In photosynthesis, the solar radiation is used to “split” water in the Calvin cycle of the chloroplasts, liberate oxygen, and fix carbon dioxide in carbohydrates, whereas other algae and some bacteria can use other photosystems to reduce in addition protons to hydrogen gas. With respect to natural photolytic processes, the important light-dependent part of the redox reactions of photosynthesis takes place at pigments, such as chlorophyll, where the oxygen atoms of water molecules are oxidized by catalyst structures containing four manganese and one calcium ions. In artificial photosynthesis, photoelectrochemical (PEC) cells utilize other metal catalyzers to overcome the high thermodynamic potential for water splitting (1.23 V under standard conditions and $\text{pH} = 0$). In thermochemical reactors, solar heat is alternatively used to split water into hydrogen and oxygen gas through redox reactions with metal catalysts at higher temperatures.

5.2 Natural Photosynthesis

In energy production, photosynthesis is the direct source of first-generation biofuels made from sugar, starch, or vegetable oil. An example is the production of bioethanol by fermentation of plant-derived sugars from sugar cane or beet. This type of biofuel has been criticized in terms of monocultivation and driver of global food shortage. In second-generation fuels, the biomass thus consists of agricultural and forest residues (e.g. stems, leaves, and husks), food-industry leftovers, or municipal biowaste. Different biochemical/biothermal processes separate

the sugar from lignin, hemicelluloses and celluloses from the woody, fibrous biomass, but they all involve glass-lined reactors and storage vessels. Particularly visible are large silos and biogas digesters of up to 7000 m³ that are frequently made from segmented steel panels glass-lined on both sides to enable easy cleaning and confer to their inner and outer sides a high resistance to acids and atmospheric corrosion, respectively.

Besides, natural water-splitting photosynthesis (biophotolysis) is an attractive route to produce H₂ gas. Processes include the use of oxygenic photosynthetic microorganisms such as genetically engineered green microalgae *Chlamydomonas reinhardtii* [15]. Large-scale algae plants are envisioned for the production of microalgal biomass and bio fuels and simultaneous capture of CO₂, comprising closed zig-zag borosilicate glass pipes and using flue gases from industry as a cheap source of sterile CO₂.

Photobioreactors have already been integrated in the envelope of buildings (e.g. as flat facade elements) not only to improve indoor air quality through O₂ production and CO₂ absorption by algae but also to grow renewable fuel stocks [16]. Such elements can span a full story. They consist of a vertical circa 80 mm-deep glass reactor panel of approximately 2.5 × 0.7 m² made up of three cavities in an aluminum frame. The central cavity has an interspace distance of 18 mm (to be filled with water and algae, serviced through the bottom edge of the panel), whereas the outer cavities are filled with argon for thermal insulation as in a standard double glazing window. The flanking glass panes of the reactor are made from low-iron soda-lime glass, which have been thermally strengthened. The outer sheets consist of a laminated safety glass to catch glass fragments in the event of reactor breakage. Laminates are made of rolled-plate glass sheets to minimize reflections (non-blinding effect) and enable an increase of solar energy gain through micro-patterns (e.g. pyramids) on the sun-exposed surface of the glass [16].

5.3 Artificial Photosynthesis

A promising technology to store solar energy is artificial photosynthesis. Different stages of integration of PV elements into electrochemical cells have been designed. The simplest, physical pathway is H₂ production by electrolysis of water with the electricity produced by PV cells. High solar-to-fuel efficiencies reaching 30% have been reported with triple-junction thin-film PV cells [17]. Depending on the sequence of electrode and semiconductor layers of such multi-junction PV cells, low-iron float-glass is used as hermetic cover in the sub- or superstrate configuration. In addition, Fresnel glass lenses are used to concentrate solar irradiation, which of course

improves the solar-harvesting part of the conversion chain.

For chemical production, the materials for light capture and the water splitting catalysts are in contact to create a wireless PEC cell. Solar radiation then induces photocatalytic reactions at the anode ($4h\nu \rightarrow 4h^+ + 4e^-$) where the oxygen of water is oxidized ($2O^{2-} + 4h^+ = O_2$), whereas hydrogen gas is generated at the cathode ($4H^+ + 4e^- = 2H_2$). Current solar-to-fuel efficiencies are relatively low as they depend strongly on suitable bandgap structures of catalysts such as TiO₂ doped with precious metals, transition metals ligated to certain organic complexes (e.g. tris(bipyridine) cobalt(II)) or bonded to chalcogenides (e.g. WSe₂). For the light-harvesting part, cells frequently include photoelectrodes made from borosilicate glasses coated with films of TCO [18]. Economically, however, much work remains to be done if the production of such PEC cells is to compete with biomass-derived fuels.

5.4 Solar Thermochemical Water Splitting

Alternatively, water can be split by chemical means, thanks to the high temperatures provided by sunlight. In a two-step cycle, a metal oxide is first reduced at high temperatures. Water is then split by oxidation of its reduced form so that the metal oxide acts as a catalyst. Temperatures of 1000–1500 °C are needed for redox-pairs such as ZnO/Zn and CeO₂/CeO_{2-δ}, which require solar concentration factors in the 1000–5000 C range with mirrors that can be arranged in dish, Fresnel, tower, and beam-down configurations. Glass is also required for the receivers, which are rotating cylinders comprising a 12 mm-thick silica-glass window 600 mm in diameter [19]. What is making this route for splitting water decidedly attractive is that the efficiency of converting solar energy into heat can reach 70% at such high temperatures.

6 Solar Water Treatments

6.1 Solar Desalination

Adequate water supply is essential for the human existence and life on Earth. Including ice, however, fresh water is a limited resource since more than 97% of it is the salty water of the oceans. As a result, coastal countries and islands in arid regions rely on sea-water desalination (e.g. Saudi Arabia, Israel). They operate multistage flash (MSF) distillation and reverse osmosis (RO) plants. The former requires heating of the brine and, thus, depends on a thermal-power station, whereas the latter consumes large amounts of electrical energy to pump sea water at

high pressures through membranes. Solar desalination with new kinds of stills thus is an emerging alternative technology for less developed countries and rural locations without access to conventional energy supply systems (gas, oil, and electricity grid). In these stills, float and rolled glass panes are used as double- or single-slope roofs to cover black-painted basins filled with saline water. After evaporation, the fresh water condenses on the inner side of the glass roof and flows toward a distillate trough where it is collected in a vessel, whereas the brine is usually drained. The average yield of distilled water depends on the different external and internal operating parameters. For a basic *passive* solar still (i.e. natural evaporation and condensation) it can reach 2–5 l/m²/d [20]. In *active* solar stills, pumps, fans, or other electrically powered devices are added to boost the performance up to 5–7 l/m²/d [20].

6.2 Solar Disinfection

In most industrialized countries the average water consumption is up to 10 times higher than the recommended basic water requirement for drinking, bathing, cooking, and sanitation services (=50 l/p/d). On the other hand, the World Health Organization (WHO) estimates that more than 1.1 billion people have no access to clean drinking water and 2.4 billion people to an improved sanitation system. For these regions WHO recommends to practice solar disinfection (SODIS), which relies on a combination of heat (infrared component) and UV-A (wavelengths 320–400 nm) of the solar irradiation to destroy bacteria cells, inter alia through pathogen damage caused by UV-A-induced reaction of oxygen to free radicals and hydrogen peroxides [21]. The technique consists in placing surface water into transparent containers, which are then exposed to the sun for a certain time on a corrugated metal roof; a minimum of six hours is recommended under sunny weather conditions to rise temperatures above 50 °C. Plain, clear white glass bottles have the advantage to be heat- and scratch-resistant and free of photoproducts. Polyethylene terephthalate (PET) beverage bottles have in contrast been recently a source of controversy because formaldehyde, acetaldehyde, and antimony appear to migrate from the bottles into fresh water [22]. The time taken for the conventional SODIS process can be greatly reduced through semiconductor-based photocatalysis, for instance, with Cu and N codoped TiO₂ [23]. Current solar reactor designs comprise a series of borosilicate glass tubes and titania-coated glass beads. The glass tubes are used as UV-A transparent containers (Figure 5) in which the transparent glass beads provide large surfaces for photocatalytic degradation of pathogens.

7 Perspectives

The use of glass will keep growing worldwide in solar-energy applications since established as well as emerging technologies require it for mechanically robust and chemically durable envelope structures at high solar-transmittance levels. For PV cells, glass thinner than 2 mm (thermally strengthened at low price) is desired to reduce the weight and to increase the photon efficiency of the modules. In addition, the demand for add-on functionalities of solar glasses is also increasing. But soiling and fouling of glass surfaces are enormous challenges, for which long-term solutions must be sought and implemented. As an example, bifunctional coatings are currently under development to combine AR with photocatalytic properties for self-cleaning [24, 25]. For photobioreactors, light conversion coatings have been introduced, which are promising to increase greatly the photosynthetic activity [26]. Along with solar shifting, integration of fluidic systems into the building envelope will be one of the strategies to gain solar energy in the future. For this application, glasses have to show not only a high optical transparency but also a chemical resistance to corrosive media with respect to architectural lifetime [27]. New concepts, like solar updraft tower plants, will require gigantic glass canopies as 5 km in diameter structures are projected for which ultrastrong glasses must be developed. Finally, with respect to solar energy conversion at higher concentration ratios ($C > 10^3$), glass that could withstand extreme temperatures (>1200 °C) for longer times is a challenge, which remains largely unresolved.

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9.5

Sulfide-glass Electrolytes for All-solid-state Batteries

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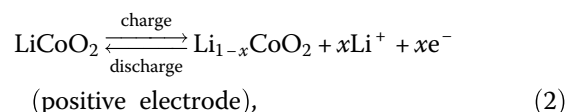
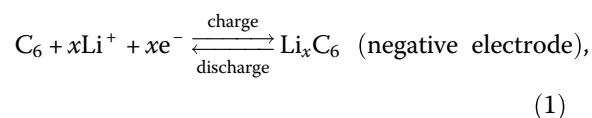
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1 Introduction

Development of high-power rechargeable batteries with an elevated energy density is being much stimulated by the rapidly growing demand for not only power-hungry mobile devices but also for automotive propulsion and distributed power-storing systems for solar energy. In this respect, Li-based batteries are potentially the most efficient since lithium is at the same time the lightest and the most electropositive metal, with a potential of -3.04 V vs. the standard hydrogen electrode [1] and, as a fast-diffusing cation, in addition generally ensures a high ionic conductivity (Chapter 4.2). Beginning in the 1970s, nonrechargeable Li cells were thus designed while fundamental research was done on reversible lithium reactions at the electrodes. Building on these practical and theoretical advances, an important step was made in 1991 by the Sony Corporation when it commercialized the first rechargeable lithium-ion battery (LIB). Since then these batteries have widely spread all over the world [1, 2] with their operating voltage of about 4 V and gravimetric energy densities of about 150 Wh/kg, which was twice or three times larger than that of the Ni-MH batteries that were hitherto prevailing.

These batteries are composed of a graphite negative electrode, a lithium transition-metal oxide (LiCoO_2) positive electrode, and an electrolyte made up of a lithium salt such as LiPF_6 dissolved in a solution of ethylene carbonate [$\text{C}_3\text{H}_4\text{O}_3$] and diethyl carbonate [$\text{C}_5\text{H}_{10}\text{O}_3$] (e.g. highly conductive and fluid carbonates, respectively, forming a nonaqueous organic solvent to prevent irreversible oxidation by water of Li into LiOH and release

of hydrogen). An appropriate interface then is simply ensured by the soaking of both electrodes into the electrolyte. Because both LiCoO_2 and graphite electrodes have a layered structure, the electrochemical reactions involved is a deintercalation/intercalation process. They can be expressed as:



with standard potentials of 3.9 and 0.1 V vs. Li^+/Li , respectively. Whereas lithium ions are efficiently mobile between the interlayers of graphite and LiCoO_2 , the structure of the electrodes does not change much upon lithium intercalation/deintercalation. Thanks to the small volume changes involved, this rocking-chair type of system ensures the long cycle lives of LIB, whether with the initial LiCoO_2 electrode or with other oxide compounds currently investigated such as LiMn_2O_4 or LiFePO_4 . But increasingly large-scale application of LIB makes its safety concerns more serious because of the rising amounts of flammable organic liquid electrolytes involved [3]. Although the energy density of LIB has been gradually increased up to 265 Wh/kg through increases of the electrode surface areas or addition of dopants to increase the electrical conductivity, realization of post-LIB with a higher energy density is still strongly desired.

On both safety and performance counts, replacing organic liquids by inorganic solids as electrolytes will be advantageous if at the same time large-capacity electrode materials can be found. Sulfur, which is difficult to use in conventional liquid-electrolyte batteries [4–6], might, for instance, be adopted for the positive electrode

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with a higher capacity than a conventional LiCoO_2 . Besides, interest has also to be paid to sodium, the alkali that is next to lithium in terms of atomic weight and standard potential and is naturally very abundant [7, 8], which is an attractive feature in large-scale applications for stationary load-leveling. In all-solid-state rechargeable batteries, direct stacking of cells in one package will in addition achieve a high operating voltage either with lithium or sodium.

Two key points to realize all-solid-state batteries are the availability of an electrolyte with high Li^+ or Na^+ ion conductivity at room temperature, along with formation of favorable solid–solid interface between the electrode and electrolyte. Now, Li^+ ion-conducting sulfide electrolytes having conductivities similar to the 10^{-2} S/cm typical of organic liquid electrolytes have recently been discovered [9, 10], whereas techniques have been developed for increasing contact area at the interface and, thus, for enhancing the utilization of electrode-active materials and rate capability.

In this chapter, these recent developments pertaining to sulfide glasses as solid electrolytes and to their application to all-solid-state lithium and sodium batteries are thus reviewed. The structure and relevant physical properties of sulfide glasses will first be briefly presented. The fundamental importance of ion conductivity and how this property can be optimized will then be described. Finally, the various ways in which good contact between the electrode and electrolyte may be designed in all-solid-state batteries will also be discussed.

2 Classification of All-solid-state Batteries

The cell voltage is determined by the difference in standard potential between the positive and negative electrodes, and its energy density by the product of this voltage and capacity. For practical purposes, the cell capacity is expressed in units of weight or of volume, including the electrolyte and both positive and negative electrodes. For research purposes, however, one usually considers the capacity referred to the weight of the targeted electrodes. Two types of all-solid-state batteries are widely studied (Figure 1).

A thin-film battery has a thin-film electrode and high charge and discharge rates because of small electrical resistances of both electrode and electrolyte. Thin-film batteries have marked advantages in terms of safety because they do not suffer from leakage and flammability. Although they have in addition long cycle lives and versatile geometries, their energy density and practical usefulness are by definition limited by the small weight of the electrode films.

Thin-film batteries are composed of electrode and electrolyte thin films prepared by RF sputtering or laser ablation. Good contact between the electrodes and electrolyte thin films is achieved by gas-phase deposition techniques. With *Lithium Phosphorus OxyNitride* (LiPON) glass electrolytes having a lithium ion conductivity with good chemical and electrochemical stability, thin-film batteries

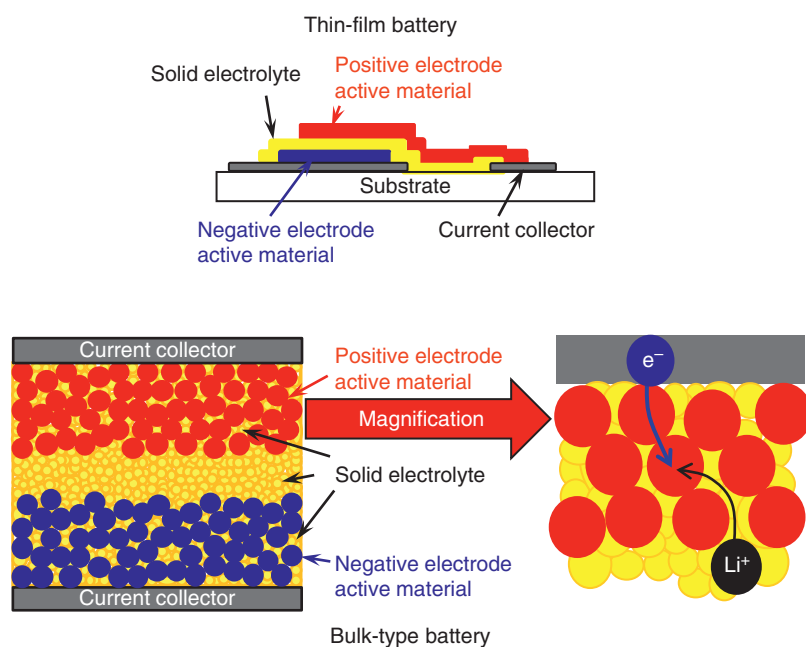


Figure 1 Comparison between the structure of thin-film (a) bulk-type (b) all-solid-state batteries.

have shown excellent long-term performances over 30 000 cycles [11]. Even though its ambient-temperature conductivity of about 10^{-6} S/cm is not so high, LiPON may be used in these batteries because one can keep the total resistance of the electrolyte small by reducing its thickness.

To increase inherently the cell capacity, use of thick electrode layers with large amounts of electrode-active materials is required. For large-size energy-storage devices with a high energy density, this combination is achieved in all-solid-state bulk batteries. For the electrolyte, particular interest has been paid to oxides and sulfides because they are well suited to satisfy five (at least) important requirements: high ambient-temperature conductivity, wide electrochemical window (i.e. voltage range where the substance is neither reduced nor oxidized), good formability (processability), favorable mechanical properties, and good chemical stability. Sulfide solid electrolytes are advantageous with respect to the first four requirements. As for the last, they do suffer from their poor chemical stability in air but this defect can be remedied by appropriate compositional adjustments.

A good electrode–electrolyte interface is easily obtained with a liquid electrolyte, but not with solid electrolytes for which intimate mixing of the two components in the form of powders must be achieved (Figure 1b). The alkali ions are then supplied from the solid electrolyte to the electrode-active material through which the electrons are mobile. Adding a conductive substance such as acetylene black (AB) to the electrode layers is, for instance, needed to ensure electron conduction pathways within electrode-active materials having poor

electronic conductivities. In practice, one fabricates bulk-type all-solid-state batteries by sandwiching a solid electrolyte layer acting as a separator between positive and negative electrode layers and then uniaxially cold pressing them at room temperature. The good electrochemical performance of Indium/LiCoO₂ batteries made in this way with Li₂S–SiS₂–Li₃PO₄ glass electrolytes were reported in 1994 [12]. Since then, as will be described, similar cells with sulfide electrolytes have been developed with better still performances.

3 Sulfide Glasses

3.1 Structure and Properties

The conductive and mechanical properties of glass electrolytes are closely related to their bonding and structure. The structure of glasses in the Li₂S–P₂S₅ and Li₂O–SiO₂ systems are, for instance, described in a similar way since addition of Li₂S causes a depolymerization of the network formed by thiophosphate PS₄^{3–} tetrahedra through the transformation of bridging into nonbridging sulfurs whose negative charge is compensated by Li⁺ ions. Owing to weaker Li–S and P–S bonds compared to Li–O and Si–O bonds resulting from the greater polarizability of the sulfide ion, however, sulfide glasses have electrical conductivities higher than those of their oxide counterparts by up to five orders of magnitude (cf. Table 1).

For the same reason, their Young moduli are typically 10 times lower. As determined from ultrasonic measurements, Li₂S–P₂S₅ glass electrolytes have a Young modulus of about 20 GPa [13]. This value is intermediate

Table 1 Li⁺ ion and Na⁺ ion conductivities for typical oxide and sulfide solid electrolytes.

Li ⁺ ion conductor			Na ⁺ ion conductor		
Classification	System	Conductivity (25 °C, S/cm)	Classification	System	Conductivity (25 °C, S/cm)
Oxide glass	60 Li ₂ O·40 SiO ₂	3×10^{-6}	Oxide glass	Na ₂ O–SiO ₂	2×10^{-7}
Oxide crystal			Oxide crystal		
NASICON	Li _{1.3} Al _{0.3} Ti _{1.7} (PO ₄) ₃	7×10^{-4}	NASICON	Na ₃ Zr ₂ Si ₂ PO ₁₂	1×10^{-3}
Perovskite	Li _{0.34} La _{0.51} TiO _{2.94}	1.4×10^{-3}	NASICON	Na ₃ Zr _{1.88} Y _{0.12} Si ₂ PO _{11.94}	2.5×10^{-3}
Garnet	Li ₇ La ₃ Zr ₂ O ₁₂	3×10^{-4}	β-alumina	Na ₂ O·11 Al ₂ O ₃	1.2×10^{-3}
Sulfide glass	75 Li ₂ S·25 P ₂ S ₅	4×10^{-4}	Sulfide glass	50 Na ₂ S·50 SiS ₂	1×10^{-5}
Sulfide crystal	Li ₁₀ GeP ₂ S ₁₂	1.2×10^{-2}	Sulfide crystal	Na ₃ PS ₄ (tetragonal)	1×10^{-6}
Sulfide	70 Li ₂ S·30 P ₂ S ₅	1.7×10^{-2}	Sulfide	75 Na ₂ S·25 SiS ₂	4.6×10^{-4}
Glass-ceramic	80 Li ₂ S·20 P ₂ S ₅	1.3×10^{-3}	Glass-ceramic	94 Na ₃ PS ₄ ·6 Na ₄ Si ₃	7.4×10^{-4}

Source: Data from [6].

between those of typical oxide glasses (Chapter 3.11) and organic polymers (Chapter 8.7). It is low enough for alkali sulfide glasses to deform elastically and, thus, to accommodate much more readily volume changes of the electrode reactions with the alkalis. As a result, most all-solid-state batteries with sulfide solid electrolytes keep good interface contact and, thus, exhibit the good cycle performance needed to ensure long cycle lives [6, 8]. Likewise, their glass transition temperatures of about only 200 °C makes them much easier to process.

Of course, the most direct strategy to increase the conductivity of glass electrolytes is to increase the number of mobile ions through an increase of the alkali-ion concentration. In the Li_2S – P_2S_5 system, the highest conductivity is achieved for the 75 mol % Li_2S composition [ortho-thiophosphate] for which the glass is composed of isolated ions of Li^+ cation and PS_4^{3-} tetrahedra. This structure is favorable for facile ion conduction, thanks to the intrinsic free volume of the glass structure.

3.2 Preparation Techniques

Sulfide-glass electrolytes are usually prepared with the quenching method. For materials with a high Li^+ ion concentration, however, quenching at a rate higher than 10^5 K/s with a twin-roller apparatus is needed to inhibit crystallization upon cooling and, thus, to expand the glass-forming region [14]. In the Li_2S – P_2S_5 system, glasses can generally be prepared in this way but the melting reaction has to be carried out in sealed quartz tubes because of the high vapor pressure of P_2S_5 at elevated temperatures. For these glasses, mechano-chemical synthesis from crystalline forms with a planetary ball-mill apparatus then is an advantageous alternative because the whole process is performed at room temperature. Fine electrolyte powders, which can be directly applied to solid-state batteries, are obtained in this manner without an additional pulverizing step [5, 6]. As an example, the 75 Li_2S ·25 P_2S_5 (mol %) glass is readily prepared via mechano-chemistry but is difficult to obtain by melt quenching. Raman spectra do indicate that the local structure around phosphorus is almost the same in glasses prepared with both methods.

3.3 Chemical Stability

A drawback of sulfide electrolytes is their low chemical stability with respect to atmospheric water. The amount of H_2S generated from Li_2S – P_2S_5 glasses in fact depends on composition. Selection of a suitable glass with a structure resisting hydrolysis is effective in suppressing H_2S gas generation [15]. Lithium *ortho*-thiophosphate Li_3PS_4 glass, for instance, has the best stability in the Li_2S – P_2S_5 system. Stability in air can also be improved by partial

substitution of oxides (Li_2O or P_2O_5) for sulfides (Li_2S or P_2S_5), but addition of Li_2O causes a monotonous decrease of the conductivity. To counter this effect, LiI has been added to Li_2O – Li_2S – P_2S_5 glasses, with the result that 30 LiI ·70(0.07 Li_2O ·0.68 Li_2S ·0.25 P_2S_5) glass has a high conductivity of 1.3×10^{-3} S/cm at 25 °C with the same chemical stability as 7 Li_2O ·68 Li_2S ·25 P_2S_5 .

Metal oxides M_xO_y (Fe_2O_3 , ZnO , and Bi_2O_3) are also efficient stabilizers because of their large negative Gibbs free energies of reaction with H_2S . Likewise, Li_4SnS_4 -based sulfide electrolytes have good chemical stability [16], especially through partial substitution of As for Sn, with which conductivities of 10^{-3} S/cm are achieved. These results conform to the HSAB theory of Pearson [17] according to which soft acids of Sn and As preferentially react with soft bases such as sulfur, rather than with hard acids of oxygen.

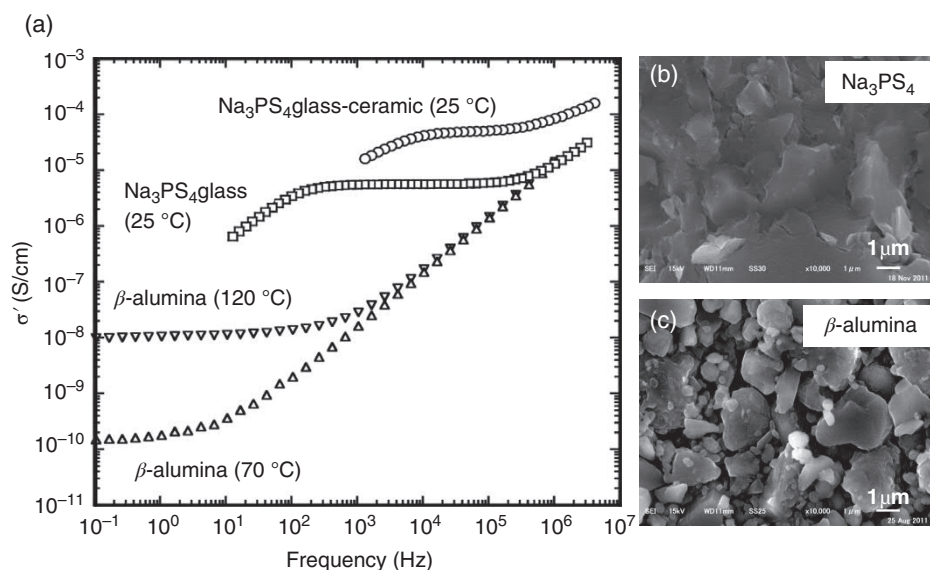
4 Sulfide Glasses as Solid Electrolytes

4.1 Electrical Conductivity

In sulfide-glass electrolytes, electrical conduction is slower at grain boundaries than in the bulk of the grains so that it varies with frequency (Figure 2), the low-frequency plateau being relevant for battery operations. The Li^+ and Na^+ ion conductivities obtained in this way at 25 °C for typical oxide and sulfide solid electrolytes are summarized in Table 1. These electrolytes are either glassy or crystalline. In general, the former show a relatively high conductivity in a wide composition range, thanks to the intrinsic free volume where the targeted Li^+ or Na^+ ions can move readily. For a given glass series the highest conductivity is then reached when the number and mobility of charge-carrier ions is maximum. In this respect, the ionic conductivity drastically increases from oxide to sulfide glasses as exemplified by the contrast between Li_2S – SiS_2 (ca. 10^{-4} S/cm) and Li_2O – SiO_2 ($>10^{-6}$ S/cm) glasses. The reason is that lithium ions, acting as a “hard acid” in the HSAB theory [17], are more mobile in a glass matrix of sulfide ions, which act as a “soft base.”

These Li_2S – SiS_2 glasses are thus attractive solid electrolytes whose conductivity can be further increased to ca. 10^{-3} S/cm by addition of either lithium halides such as LiI or lithium *ortho*-oxosalts such as Li_3PO_4 or Li_4SiO_4 . That lithium sulfide solid electrolytes have a unity transference number is another advantage: although commercially available organic liquid electrolytes show room-temperature conductivities of 10^{-2} S/cm, their lithium transference number is lower than 0.5. With a similarly high ion conductivity of 10^{-2} S/cm, lithium sulfide electrolytes are thus preferable for high-rate rechargeable batteries.

Figure 2 Relationship between the electrical conductivity and the microstructure of glass-ceramics. (a) Frequency dependence of the room-temperature conductivity (σ') of Na_3PS_4 glass and glass-ceramic electrolytes, the apparent decrease at the lowest frequencies being due to electrode polarization. Conductivities for a powder-compressed pellet of β -alumina at 70 and 120 °C are included for comparison. (b) and (c) Cross-sectional SEM images for powder-compressed pellet of Na_3PS_4 glass-ceramic and β -alumina, respectively.



4.2 Conductivity Optimization

In contrast, the conductivity of crystalline electrolytes strongly depends on the crystal structure so that it is highest for well-defined chemical compositions and heat treatments. A conductivity of more than 10^{-3} S/cm is, for instance, found in $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_{2.94}$ perovskite, whereas that of sulfides such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ is higher than 10^{-2} S/cm. Thanks to such elevated values, the maximum conductivity of 10^{-3} S/cm of sulfide-based glasses at room temperature can be increased through partial crystallization [5, 6]. In Li^+ ion conductors, heating of 70 Li_2S :30 P_2S_5 (mol %) glass at 240 K causes $\text{Li}_7\text{P}_3\text{S}_{11}$ to precipitate as a primary phase. The resulting glass-ceramics has a conductivity higher than 10^{-3} S/cm. Upon further heating at 360 °C, the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystallinity increases so that, under optimum synthesis conditions, a conductivity of up to 1.7×10^{-2} S/cm at 25 °C can be achieved [10]. Importantly, however, higher temperatures are to be avoided as $\text{Li}_7\text{P}_3\text{S}_{11}$ completely decomposes upon heating up 550 °C: thermodynamically stable phases such as $\text{Li}_4\text{P}_2\text{S}_6$ then form and cause a conductivity decrease.

With the metastable $\text{Li}_{3.25}\text{P}_{0.95}\text{S}_4$ phase (thio-LISICON $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ analog) as a solid electrolyte, the 80 Li_2S :20 P_2S_5 (mol %) glass has by comparison a conductivity of 10^{-3} S/cm, which is lower than that of the aforementioned 70 Li_2S :30 P_2S_5 glass-ceramics. This contrast highlights a basic difference between electrolytes made up of glass-ceramics, whose conductivity is strongly related to their crystalline phases, and those made up of glasses, where it simply depends on the lithium ion concentration. As determined by Rietveld analyses of synchrotron XRD measurements, $\text{Li}_7\text{P}_3\text{S}_{11}$ has a triclinic unit cell with the $P-1$ space group and is made up of

P_2S_7 ditetrahedra and PS_4 tetrahedra similar to those of the Ag^+ ion conductor $\text{Ag}_7\text{P}_3\text{S}_{11}$ (monoclinic, space group C2/c). The lithium atoms are located around the P_2S_7 ditetrahedra and PS_4 tetrahedra are surrounded by three to five sulfur atoms. By heating a supercooled liquid of glass electrolyte, one tends to precipitate as a primary crystal either a metastable or a high-temperature phase with a high conductivity.

A high-temperature α -AgI phase with an extremely high Ag^+ ion conductivity is also stabilized at room temperature by crystallization of AgI-based oxyhalide glasses [18]. Glass electrolytes are thus quite useful as precursors for precipitating superionic crystals, which are difficult to synthesize by conventional solid-state reactions.

If the conductivity is lower for Na^+ - than for Li^+ -ion glasses (Table 1), the opposite holds true for crystals with *Na* Super Ionic Conductor (NASICON)-type structures. As an example, the NASICON phases $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ and $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ have Na^+ - and Li^+ -ion conductivities of 10^{-3} and 7×10^{-4} S/cm, respectively. But studies of sulfide crystalline materials with Na^+ -ion conduction are still limited so that improvements can be expected. Although tetragonal Na_3PS_4 has, for instance, a conductivity of only 10^{-6} S/cm, cubic Na_3PS_4 has been precipitated from Na_3PS_4 glass to form a glass-ceramic electrolyte with a much higher conductivity of 4.6×10^{-4} S/cm at 25 °C. In addition, replacement of 6 mol % Na_3PS_4 by Na_4SiS_4 further increases the conductivity to 7.4×10^{-4} S/cm at room temperature. This value is the highest achieved for Na^+ ion conduction in sulfide materials reported so far, presumably as a result of the creation of interstitial Na^+ ions by partial substitution of Si^{4+} for P^{5+} in the network. Detailed structural analyses of the precipitating crystals are thus needed to optimize the conductivity of glass-ceramic electrolytes.

4.3 Electrochemical Window

Of particular interest is the electrochemical window (Chapter 5.10) wider than 5 V measured by cyclic voltammetry for $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramic electrolytes. To determine it, a stainless-steel disk acting as a working electrode and a lithium foil working as a counter electrode are attached on each face of a pelletized 70 Li_2S :30 P_2S_5 glass-ceramics. A cathodic and an anodic current flow caused by lithium deposition and dissolution, respectively, are observed reversibly at around 0 V (vs. Li^+/Li). Notwithstanding the current caused by this dissolution/deposition process, no current is observed over the whole -0.1 to 5.0 V range. Hence, the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramic electrolyte is not prone to oxidation decomposition and shows good compatibility with lithium deposition and dissolution.

4.4 Formability

Good contact at the solid-solid interface between the electrode and electrolyte is a key to improving the performance of all-solid-state batteries. In this respect, too, sulfide electrolytes are advantageous in terms of grain boundaries and solid-solid contacts achieved without any heat treatment. By only cold pressing, a 90% relative density is, for example, achieved at a pressure of 360 MPa when starting with 75 Li_2S :25 P_2S_5 (mol %) pellets. The material is made up of lithium (Li^+) and thiophosphate ions (PS_4^{3-}), which are thought to diffuse at the particle boundaries so as to increase grain size, reduce voids and eventually make grain boundaries hardly visible once densification is achieved through this *room-temperature pressure sintering* process [8].

The importance of this effect is shown by a comparison (Figure 2) made between the conductivities of pressure-sintered Na_3PS_4 glass-ceramics with those of Na_3PS_4 glass and β -alumina, a typical Na^+ ion conductor. For this last material, the low-frequency conductivity of sintered pellets is 1.2×10^{-3} S/cm at 25 °C (Table 1) and that of simply compressed powders is many orders of magnitude lower at 70 and 120 °C (Figure 2) and cannot even be measured at 25 °C. The reason is that one cannot reduce the grain-boundary resistance at room temperature, but need to sinter the material above 1000 °C. The advantage of the Na_3PS_4 glass-ceramic is thus obvious since in the form of compressed powders its conductivity is 10^{-4} S/cm at 25 °C and further increases at temperatures of 70–120 °C. This difference between β -alumina and Na_3PS_4 glass-ceramics clearly correlates with the poor and excellent grain contact visible in the former and latter, respectively (Figure 2).

In this respect, glass electrolytes have the important advantage of ready softening at temperatures close to

glass transition. At such temperatures grain boundaries and voids almost disappear in a 80 Li_2S :20 P_2S_5 (mol %) glass upon compaction, causing the room-temperature conductivity to increase to 8.8×10^{-4} S/cm from the 3.7×10^{-4} S/cm of a cold-pressed sample.

5 Bulk-type Batteries with Sulfide Electrolytes

5.1 Electrodes

In commercially available lithium-ion batteries, the positive and negative electrodes are typically LiCoO_2 and graphite, respectively, but spinel-type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is also used as a negative electrode. These materials remain used in all-solid-state batteries. As an example, In/ LiCoO_2 or Li-In/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells with a $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramic electrolyte operated as a rechargeable battery at 25 °C under a limited current density of 0.064 mA/cm² keeps a charge-discharge efficiency of 100% for several hundred cycles [5]. Under a current density higher than 10 mA/cm², a discharge-charge capacity of about 140 mAh/g has been maintained in the latter cell at 100 °C without degradation for 700 cycles [5]. As the sulfide-glass-ceramics is thermodynamically stable at 100 °C, the cell resistance decreases and the rate performance is thus improved with an increase in operating temperature.

All-solid-state sodium cells with Na_3PS_4 glass-ceramic electrolytes also operate as a rechargeable battery at room temperature [8, 19]. An Na-Sn alloy is used as a negative electrode and transition metal sulfides such as TiS_x as a positive electrode. Sodium cells with amorphous TiS_3 have a capacity of 300 mAh/g, which is three times higher than that of crystalline TiS_2 (a typical positive electrode-active material), and retain this capacity for several cycles. Thanks to its structural flexibility and free volume, amorphous TiS_3 electrodes are thus effective for intercalation of both sodium and lithium ions in all-solid-state cells.

In summary, bulk-type solid-state cells inherently exhibit an excellent cycle performance and high-rate operations at elevated temperatures at which conventional lithium-ion batteries with organic liquid electrolytes are difficult to use.

5.2 Interfacial Resistance

A problem encountered in electrolyte-electrode contacts is that an interfacial resistance manifests itself after the initial charging process. For a LiCoO_2 electrode and a $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ electrolyte, coating of the electrode particles by Li^+ ion-conductive oxide films such as LiNbO_3 on LiCoO_2 is, for instance, an effective way to decrease this resistance and, thus, to enable cell operation at current

densities higher than 1 mA/cm^2 [20]. When examined by cross-sectional TEM-EDX techniques (Chapter 2.3) after charging, the electrode–electrolyte interface shows the presence of an interfacial layer. Acting as buffer layers, the coatings could then either suppress it or inhibit its formation [21]. Surface coating of active material particles with oxide thin-films thus is useful to improve the rate capability of all-solid-state batteries [20, 21], but the effect requires coating with high-conductivity ions. As an example, one reduces more effectively the interfacial resistance by coating with a $\text{Li}_{3.5}\text{Si}_{0.5}\text{P}_{0.5}\text{O}_4$, whose conductivity is 10^{-6} S/cm than with Li_2SiO_3 or SiO_2 .

Likewise, CoS or NiS coatings on LiCoO_2 decrease the interfacial resistance after charging. These metal sulfide coatings also act as buffer layers that suppress degradation at the highly reactive interface between charged LiCoO_2 and the Li_2S – P_2S_5 electrolyte. This result implies that cobalt sulfides, which are presumably interfacial compounds, do not cause the interfacial resistance but rather the degradation of the solid electrolyte and/or the LiCoO_2 electrode at the interface. Although the influence of a space charge layer on the interfacial resistance remains to be clarified, structural deterioration at interfaces after cycling is actually observed, which is a main cause of the increase in the interfacial resistance.

6 Interfacial Design

As already noted, electrode–electrolyte interfaces must be suitably designed for ensuring effective charge-transfer reactions and, thus, good charge–discharge performances of all-solid-state batteries. Increasing the contact area between the electrode and electrolyte is needed to achieve larger capacity. Three approaches can be followed in this respect (Figure 3).

6.1 Surface Coating of Solid Electrolyte on Active Material Particles

To achieve large contact areas between the Li_2S – P_2S_5 solid electrolyte and the LiCoO_2 active material, the former can be coated on the latter by pulsed laser deposition (PLD). The resulting decrease of the solid electrolyte content is useful for increasing the energy density of solid-state cells. As an example, coating of LiCoO_2 particles with a 80 Li_2 ·20 P_2S_5 (mol %) solid electrolyte is carried out by PLD with a KrF excimer laser ($\lambda = 248 \text{ nm}$) as sketched in Figure 3a. A pelletized mixture of Li_2S and P_2S_5 crystalline powders was used as a target whereas the LiCoO_2 particles were first coated themselves with

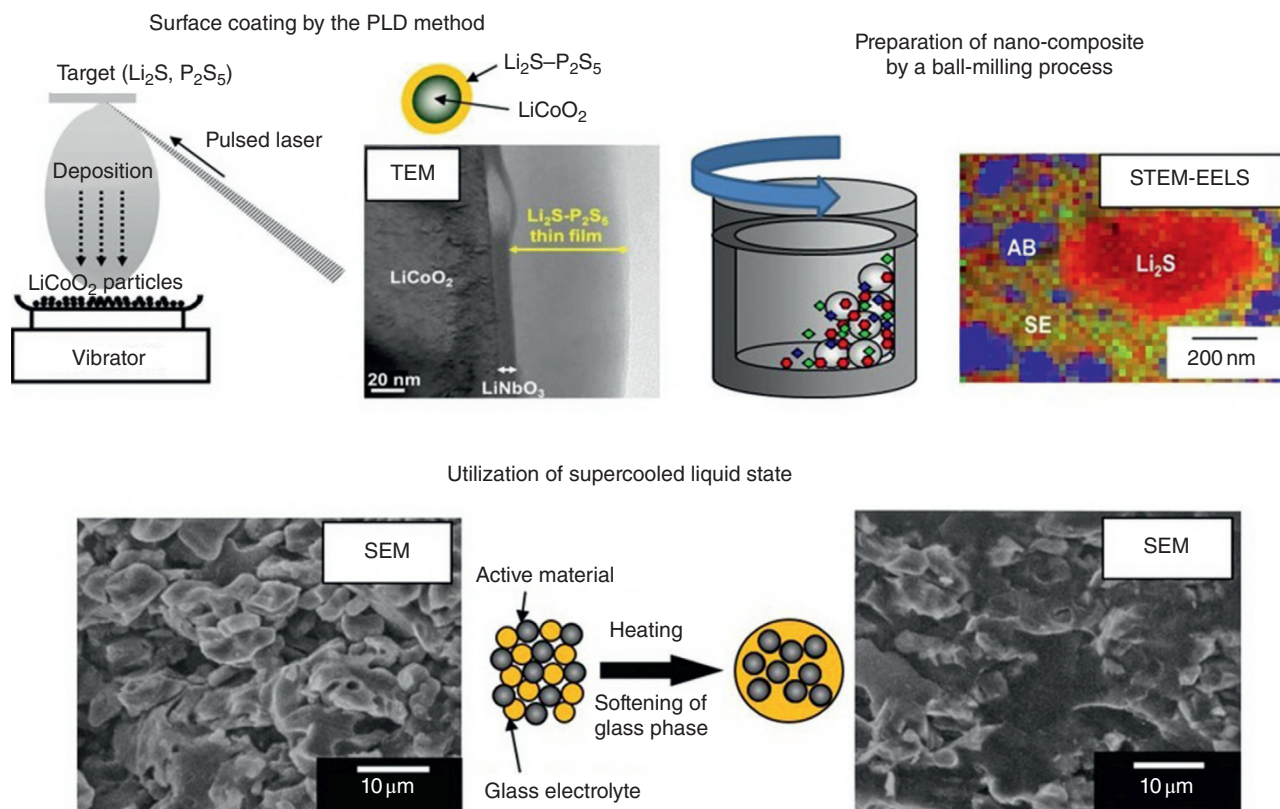


Figure 3 Sketch of three procedures used to ensure favorable electrode–electrolyte interfaces.

LiNbO₃ film to decrease the interfacial resistance after charging. During the deposition, the LiCoO₂ particles were fluidized by a vibrator in order to form a uniform solid electrolyte layer on them. According to the cross-sectional TEM image of Figure 3a, this film has a thickness of about 70 nm and shows good adhesion to the surface of the LiNbO₃-coated LiCoO₂ particles. Its conductivity is about 10⁻⁴ S/cm at 25 °C.

The In/80Li₂S-20P₂S₅ glass-ceramics/LiCoO₂ cells prepared in this way can be charged and discharged and retain their initial capacity for several cycles, whereas similar cells with noncoated electrodes do not work because of insufficient lithium ion conduction pathways to LiCoO₂. Another advantage of the process is the 3 wt % solid electrolyte coating in the LiCoO₂ working electrode, which allows the energy density of the cell to be increased up to ca. 280 Wh/kg (normalized by the weight of LiCoO₂ positive electrode layer). For comparison, without coating one needs to add 30 wt % solid electrolyte particles to operate typical solid-state In/LiCoO₂ cells, in this case with a lower energy density of ca. 230 Wh/kg.

Alternatively, favorable electrode–electrolyte interfaces can be more simply obtained from liquid-phase synthesis of the electrolyte. From the reaction of Li₂S and P₂S₅ in a mixture of *N*-methylformamide [C₂H₅NO] and *n*-hexane [C₆H₁₄], a yellow solution is obtained (Figure 4) which, upon mixing with LiCoO₂ particles and drying at 180 °C for three hours under vacuum, yields electrodes with a 7.5 wt % solid electrolyte coating [22]. Without addition of solid electrolyte and conductive additive particles to the positive electrode, a cell made in this manner is rechargeable with an initial discharge capacity of 32 mAh/g. This value is still small at the

present stage because the solid electrolyte has a low conductivity of about 10⁻⁶ S/cm, but work is underway to improve the situation.

6.2 Ball-milling Prepared Nanocomposites

As already noted, high-energy planetary ball-milling is often used for preparing nanocomposite electrolytes. In particular, one obtains favorable interfaces between the solid electrolyte and the active materials with the help of conductive additives such as nanocarbon materials to improve the low lithium and electronic conductivities. Sulfur and Li₂S are attractive positive electrode materials with theoretical high capacity of 1672 and 1170 mAh/g, respectively. The latter compound is a discharge product of the sulfur-active material as described by the reaction $S + 2Li^+ + 2e^- \leftrightarrow Li_2S$. Like LiCoO₂, Li₂S is a lithium source so that its use as a positive electrode should be advantageous in terms of battery versatility and cycleability when combined with a Li-free negative electrode material such as graphite. Both sulfur and Li₂S are insulators, however, so that nanocomposites with carbon conductive additives should be needed to incorporate these active materials.

Recently, sulfur and Li₂S have been studied for Li/S batteries with high energy density, but the use of these active materials is difficult because the electrochemically formed lithium polysulfide (Li₂S_x) species easily dissolve in conventional organic liquid electrolytes. Such a reaction does not take place in solid electrolytes, as illustrated by a mixture of Li₂S active material, Li₂S–P₂S₅ solid electrolyte, and AB (conductive additive) ground with a planetary ball-mill apparatus. The cross-sectional STEM-EELS mappings reveal that the particles form a nanocomposite material where Li₂S (ca. 200 nm in size) and AB (ca. 100 nm in size) domains are dispersed and embedded in the solid electrolyte matrix (Figure 3).

The charge–discharge curves of all-solid-state cells with S or Li₂S active material at 25 °C under a current density of 0.064 mA/cm² are shown in Figure 5. The weight ratio of S or Li₂S, Li₂S–P₂S₅ solid electrolyte, and AB are 25 : 50 : 25. The Li-In/S cell exhibits a large reversible capacity of over 1500 mAh/g of sulfur with an average potential of ca. 2.1 V (vs. Li⁺/Li). Similar charge–discharge profiles are observed in the In/Li₂S cell. The reversible capacity is lower than that of the Li-In/S cell because of smaller theoretical capacity of Li₂S. The charge–discharge curves of a typical all-solid-state In/LiCoO₂ cell are also shown in Figure 5. The cell with a sulfur electrode shows a capacity 15 times higher than that with LiCoO₂, although the operating potential of the former is almost half that of the latter, since the energy density is the product of the cell

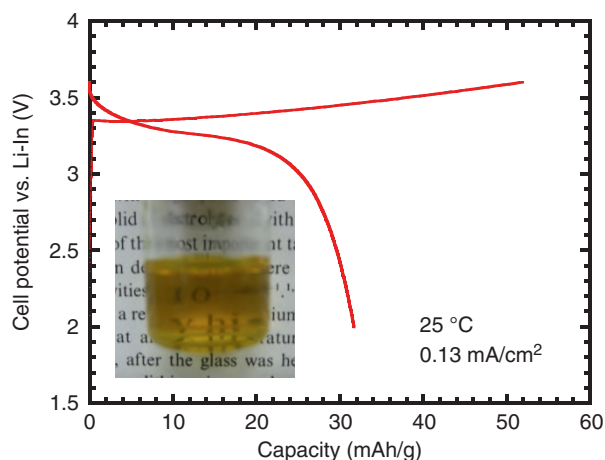


Figure 4 Initial charge–discharge curves of all-solid-state In/LiCoO₂ cells using solid electrolyte-coated LiCoO₂ via *N*-methylformamide solution. Inset: photograph of the NMF solution prepared from Li₂S and P₂S₅.

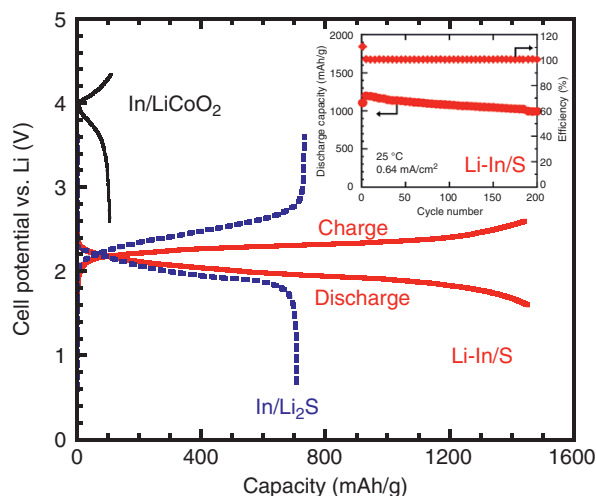


Figure 5 Charge–discharge curves of all-solid-state Li-In/S and In/Li₂S cells at 25 °C under the current density of 0.064 mA/cm². Curves for the cell with a typical positive electrode of LiCoO₂ are also shown for comparison. Inset: cycle performance of the Li-In/S cell at a higher current density of 0.64 mA/cm².

capacity and operating potential. In Figure 5, the inset shows the cycle performance of the Li-In/S cell at 25 °C under a higher current density of 0.64 mA/cm². Good cycleability at 25 °C is apparent. The capacity still is 1000 mAh/g after 200 cycles, suggesting that the use of solid electrolyte is essentially useful for developing Li/S batteries with high energy densities and long cycle lives. The charge–discharge mechanism of the In/Li₂S cell has been explained in terms of TEM observations [23] according to which a high capacity is thanks to reversible reaction between crystalline Li₂S and amorphous sulfur in the positive electrode.

6.3 Use of the Supercooled Liquid State

As already noted in Section 4.4, the softening technique ensures good contact at the electrode–electrolyte interface, thanks to the viscous flow of the supercooled liquid electrolyte onto the electrode-active materials. Upon cooling to room temperature, the contact is maintained, as shown by SEM micrograph cross sections of a pelletized mixture of LiCoO₂ and Li₂S–P₂S₅ glass (Figure 3c) kept at 210 °C for four hours. As compared with observations made on the sample before heat treatment, these images do indicate that the grain-boundaries and pores among the LiCoO₂ particles are filled with softened glass domains. That an all-solid-state cell with a heat-treated LiCoO₂ electrode exhibits a larger reversible capacity than a cell without heat-treatment thus is readily accounted for.

7 Perspectives

Commercial production of all-solid-state batteries is not expected before the early 2020s because it still requires to improve both the conductivity and electrochemical–chemical stability of sulfide electrolytes. In addition, facile approaches for achieving favorable electrode–electrolyte interfaces are needed. A solid-electrolyte coating technique via a liquid-phase process is a cost-effective route to form close interfaces with large contact areas. Further studies about suitable solvents and reaction mechanism are thus required. The control of the size, morphology, and dispersibility of both solid electrolyte and electrode-active material particles are also important for assembling large-sized and stacked batteries. With respect to natural resources and cost, sodium would be advantageous since it is the sixth most abundant element in the Earth’s crust with an abundance of 2.63 %, which is 660 times larger than that of Li [2]. All-solid-state sodium-sulfur batteries with Na₃PS₄ solid electrolyte consisting of only the abundant elements Na, P, and S are fascinating rechargeable batteries from the viewpoint of long-term availability of elements. Our preliminary experiments give a possibility of all-solid-state Na/S batteries with a large capacity of ca. 1200 mAh/g of sulfur-active material at room temperature. Room-temperature operating Na/S batteries would meet a demand for grid application and distributed storage at individual houses. All-solid-state Li or Na batteries with high energy density may replace lithium-ion batteries because of their intrinsic high safety and good cycleability, which meet the demands of large-sized rechargeable batteries for electric cars and distributed power sources at individual houses. But further development in both materials and fabrication technology is needed for commercialization of such solid-state batteries.

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9.6

The World of the Flat-glass Industry

Key Milestones, Current Status, and Future Trends

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1 Introduction

Flat glass has long been segmented into plate and sheet types. Traditionally, the former was cast and then ground and polished whereas the latter was made with the cylinder and crown processes, which were eventually replaced by drawn processes in the early twentieth century (Chapter 10.9). As developed in Britain by Pilkington Brothers in the 1950s, float glass revolutionized the flat-glass industry (Chapter 1.4). When the process became widely licensed in the early 1960s, it quickly dominated the market in developed countries at a time when a rapidly growing demand made economically not too costly the switch to the new technology from the old processes, which had become obsolete for most purposes.

Nowadays, flat glass is utilized not only in windows and facades for buildings but also in a variety of end products such as windscreens and windows for transportation vehicles, furniture and appliances, solar panels, and many other applications among which electronics is currently sustaining an extremely strong growth. Some of these applications have specific requirements, for instance, a maximum transparency for solar cells (Chapter 9.4) or a thickness of a fraction of 1 mm for the various glass plates of display panels (Chapter 6.10), which has made room for the development of other processes (Chapter 1.4).

In this respect, the important point is that this evolution has taken place at an unprecedented rate. In parallel, new companies have emerged as a result of the very strong economic growth of Asia. The purpose of the present chapter thus is to review the rapidly changing situation and the economic challenges it is raising. Although the main features concerning the history of

the fabrication of flat glass are discussed in detail in another chapter (Chapter 10.9), it will be useful first to summarize them to put the long-term evolution of the processes in perspective. The impact of the float-glass revolution will then be reviewed and conjectures about the future of the flat-glass industry be presented.

2 A Short Overview: Processes and Products

2.1 From the Beginnings to the Mid-nineteenth Century

Some important early steps in glassmaking are summarized in Table 1. The remains of flat-glass panels made 20 centuries ago have been found in houses at Pompeii and Herculaneum (Chapter 10.3). The mediocre quality and high cost of the cast glass used for this purpose prevented its extensive use; however, in contrast to the vessels of any shape and size that came to be widely produced after the very first revolution in glassmaking represented by the invention of blowing toward the beginning of our era (Chapter 10.3). Hence, it was only with church windows that much later flat glass became common in the Middle Ages in the form of stained glass made not too far away by the crown or cylinder processes (Chapter 10.8). Italy, and particularly Venice, then played a key role in the development of the flat-glass industry when, during the Renaissance, mirrors were produced with a tin-mercury amalgam as a reflecting layer. For cost reasons, however, house windows were not widely equipped with flat glass before the eighteenth century in Western Europe.

In the early nineteenth century, the Industrial Revolution provided larger quantities of flat glass across Western Europe. The 1851 “Crystal Palace Exhibition,” in London, specially stimulated the glass industry with its gigantic

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W. Klingensmith, Business Development, PPG Performance Glazings
International, Pittsburgh, Pennsylvania, USA

Table 1 Early key technological milestones for flat glass.

Date	Innovation	Place
First century BCE	Glass blowing	Middle East
First century	Glass windows at Pompeii	Italy
First century	Production of flat glass by cylinder and crown processes	Europe
Eleventh century	Glass for cathedrals and abbeys – church windows	Europe
Twelfth century	Venetian regulation of glass trade	Italy
Fifteenth century	Cristallo – clear glass at Venice	Italy
1500s	Venetian mirrors	Italy
1612	<i>L'Arte Vetraria</i> , by Antonio Neri (1576–1614)	Italy
1615	Replacement of wood by coal as a combustible	England
1688	Table cast glass by Bernard Perrot [Perotto]	France
1791	Leblanc process for production of soda ash (first revolution)	France

Table 2 Key technological milestones from the mid-eighteenth to the mid-nineteenth century.

Date	Innovation	Place
1840	Silver replacing mercury-tin amalgams for mirrors	UK
1851	Crystal Palace (London)	UK
1860	Stetson patent for double-pane insulating glass	USA
1863	Solvay process improving soda ash production	Belgium
1867	Siemens continuous furnace (second revolution)	UK
1870	De la Bastie process for tempered glass	France
1898	Wired glass “Georgian Wired Glass”	UK
1905	Fourcault sheet process (third revolution)	Belgium
1910	Bicheroux process (glass rolled between rollers)	Germany
1900s	First windscreens for automobiles	—
1910s, 1920s	Safety glass (laminated and tempered)	Europe, USA
1917	Colburn (Libbey Owens) sheet process	USA
1920s	Perception of glass as a modern material	Europe
1925	Pittsburg process for Pennvernon sheet glass	USA
1935	Twin (continuous grinding and polishing on both faces)	UK
1940	First patent on pyrolytic coatings	USA
1940	Fabrication of double-pane insulating glass	USA, Europe
1959	Float by Pilkington (fourth revolution)	UK

greenhouse-like building that covered almost 20 acres (about 81 000 m²) and used some 400 tons of sheet glass [1]. At the same time, the rate of innovation increased tremendously as seen by even a quick comparison between the lists of Tables 1 and 2. Of course, it was the increasing demand for flat glass that initially drove these innovations, which in turn increased the demand for glass as a result of the better quality and lower price that they ensured and of the new applications they made possible.

Of particular interest has been a series of four additional revolutions that transformed the production of flat glass by making, in particular, possible its *continuous* production: (i) the industrial fabrication of pure soda ash, which replaced the lower-quality product obtained from the combustion of plants; (ii) the Siemens continuous furnace, which drastically changed the melting process; (iii) the Fourcault drawn-sheet process, which was the first to provide a continuous ribbon of flat glass; and

(iv) and finally the float process, which provided a fire-polished flat glass ribbon with parallel faces of uniform thickness can now be produced with thicknesses ranging from 0.4 to 25 mm.

In spite of the success it met, however, the float process has not completely prevailed. Flat glass in effect is still produced by the cast process in the form of patterned, rolled, or textured panes. At the exit of a melter (furnace), the melt flows under a refractory gate that controls its thickness and speed before being patterned and textured on one side, while remaining smooth on the other. Today, this glass is mainly utilized in decorative, privacy

management, and solar glazing applications, for which it is often utilized instead of float glass. Patterned glass is also used as building glazing in some developing countries.

2.2 Latest Key Milestones

That the rate of innovation has kept accelerating in the last past half-century is clearly apparent in the lists of Tables 3 and 4. These items are both self-explanatory and much too numerous to be commented individually. It will rather suffice to note that five sectors are currently

Table 3 Key milestones from the 1960s to 2014 in process and product development.

Date	Change	Place
1959	Float by Pilkington (fourth revolution)	UK
1960s	Pilkington licenses in Europe and North America	Europe, USA
1970s	Batch coaters	Europe
	Tempering on horizontal furnace	World
	Structural glazing (sealed)	Europe, USA
	Step-by-step termination of sheet-glass production lines	World
	Insulating glazing in buildings as a result of energy crisis	Europe, USA
1980s	Large development of coatings (with magnetron coaters)	World
	Jumbo size becoming standard in Europe	Europe
	Bendable and temperable coatings (vacuum deposition)	USA
	Structural glazing (bolted glass)	Europe
	Extra-clear glass (beginning with the Louvre Pyramid)	Paris
1990s	End of Pilkington license: newcomers in the production of flat glass, large increase of production lines	World
	Warm edge for IG unit spacers	Europe, USA
	Oxy-fuel burners	USA
	Structural glazing (beams and large sizes)	Europe
	Hydrophobic coatings	
2000s	Easy maintenance coatings ("self-cleaning")	World
	China becoming first flat-glass producer in the world	World
	Low-iron glass for photovoltaic cells	World
	More stringent European standards instead of ASTM's	World
	Head-up displays on cars	USA
	Summer comfort becoming a focus	Sunny regions
	Passive houses – Zero Energy Building	USA, Europe
	Very large glazings (e.g. Shanghai Apple store)	Asia
	Complex shapes, glazing deformation on building included	World
	Insulating-glass units with U values of $\sim 0.5 \text{ W/m}^2\text{K}$	World
1980–2010	Thin glass for communication tools becoming new niche (some float lines producing only glass for LCD)	Asia
	Continuous price decreases in USA and Europe	USA, Europe

Table 4 Key improvements from 1962 to 2014 on coatings, tempering, laminating, and insulating glazing.

Product	Key improvements from 1962 to 2014
Float glass	- Availability of 2 mm-thick float glass in 1970 - Development of extra-clear glass from the mid-1980s (for architecture, furniture, appliances, and solar) - Development of extra-thin glass from late 1990s (for communication devices) - Larger furnaces: 1000–1300 tons per day vs. 400–500 in the 1960s - Longer furnace lifetimes: 12–18 years vs. 5 in the 1960s - Notable improvements in productivity (ton per worker unit and per year) and energy (spent per ton of saleable glass) - Usage of oxy-fuel combustion for some furnaces - Notable improvements in reduction of environmental pollution
Coated glass	- Magnetron cathodes - From batch to “on-line” process - Pyrolytic coaters dominant in the 1970s replaced by sputtering coaters from the mid-1980s (up to 10^7 m²/yr) - Temperable coatings (sputtering deposition) - Hydrophobic coatings - Low-maintenance coatings - Coatings with double and then triple silver layers - Coatings matching requirements for summer comfort - Commercial development of electrochromic coatings - Coatings for faces 1 and 4 of insulating glazings
Tempered glass	- From vertical to horizontal tempering - Notable improvement of optical properties of tempered glass - Huge productivity increase of tempering production lines - Tempering of 18 m-long glass parts in large production lines
Laminated glass	- Large demand of laminated glass for safety and security - Poly vinyl butyral (PVB) films for sound insulation - Head-up displays - Laminating of 18 m-long glass parts in large production lines - New films in addition to the extensively used PVB
Insulating glass	- Up to mid-1970s large portion of glazings are single panes - Insulating glass with single, then double sealant - Double insulating glass with low-e coating becoming standard - Argon filling becoming standard in some countries - Warm-edge technologies to reduce overall u-values - Triple insulating glass - Moving from 5.6 (single glazing) down to 0.5 W/m² °C
Glazings	- Structural glazing participating in strength of whole structure - Very large sizes - Very complex shapes - Cold bending of glazings, on building

the bigger users of flat glass (Table 5): construction (for windows and mirrors in either new or renovated buildings); car and, more generally, transportation vehicles (again for original equipment or replacement of safety

windows); appliances and furniture; solar energy (photovoltaic and concentrated power); and electronics-communications. For some or all of these sectors, insulating, tempered, laminated, or coated products have been

Table 5 Main usages of flat glass.

Business		% (volume)
Building	New building	35
	Refurbishment	35
	Interior	13
	Total	83
Other	Solar energy	2.5
	Others	7
	Total	9.5
Automobile	Original equipment	6
	Aftermarket	1.5
	Total	7.5
Grand total		100

Table 6 Key figures about flat-glass products.

Global market	Figures
Flat glass	70 million tons per year 7000 million m ² (equivalent 4 mm)
Low-emissivity glass	450 million m ² per year
Laminated glass	300 million m ² per year
Coaters lines	Several hundreds
Tempering lines	7 000 to 10 000

Best guesses for 2014.

key factors for their markedly increasing uses of glass (Table 6).

To quote a first example, horizontal tempering eliminated the so-called tong marks of the vertical process, which has greatly facilitated the penetration of tempered products into the transportation and building markets, thanks also to an improved productivity combined with a better product quality. But a more instructive case perhaps is that of insulating glazing, which was first adopted by the transportation industry, mostly for train cars, in the 1950s and 1960s. After the energy crisis of the 1970s, the energy savings often requested through national codes induced a systematic implementation of insulating glass in the building sector. A large-scale development of coatings quickly followed in the 1980s, facilitated by the efficiency of low-emissivity coatings for energy savings (Chapter 6.7), which allowed large coaters to be made at a competitive price. At the same time, concerns for safety, security, thermal comfort, and noise reduction led to the development of insulating glazings incorporating not only

coated but also tempered and laminated glass. As a matter of fact, transportation continues to be a key driver of product development for the flat-glass industry. Although remaining a relatively minor user of flat glass in terms of volume (Table 4), it represents an important source of added value (Chapter 9.2).

Since coatings are now standard in a great many products, it is worth to remind that glass producers generally agreed in the 1960s and 1970s that pyrolytic processes would become dominant. By a twist of history, however, in the following decade the advantage shifted to sputtered coatings. Also widely used today in the building industry, temperable sputtering coatings were first developed for windscreens with a noticeable development conducted by PPG [2]. These coatings are in general less expensive, offer a wider range of features as well as often better optical and energy properties, and in addition are overcoming two weaknesses of pyrolysis processes in terms of durability and temperability. These advantages are reflected in the dramatic increase of the US sales of reflective coatings, which went from 15 000 and 270 000 m² in 1967 and 1970, respectively [3], to a current value of about 500 million m².

As for the latest developments, they concern extra-clear glass for the solar industry (mainly photovoltaics) and extra-thin glass for communication devices (telephones, tablets, and flat display panels) whose production has tremendously increased since the beginning of the 2000s.

Finally, another significant trend is that until the 1960s most of the development of new products was conducted by the producers of flat glass. Catalogs from PPG in the 1940s [4] or of Saint-Gobain [5] in the 1950s and 1960s exemplify very well the implication of flat-glass producers in product design. Today, in contrast, most of the development of new products is performed by the downstream fabricants or, for the building industry, by facade companies (Chapter 9.1). Likewise, equipment for glass processing has also been developed during that period of time by new, dedicated companies.

3 The Float-glass World

3.1 The Age of Float Glass

To assess better the current evolution of the flat-glass market, it should be noticed first that until recently the main producers were rather “old” companies funded in the nineteenth or early twentieth century to produce window and/or plate glass (Table 7). One could even state that the flat-glass industry is a very rare example of a sector where old-age companies have been able to keep dominant positions in the midst of continuous

Table 7 Foundation of some of the key flat-glass companies.

Date	Companies
1665	Saint-Gobain (France) Incorporation of its European subsidiaries in the 1980s and 1990s (Saint Roch [Belgium], Vegla [Germany], Cristaleria Espanola [Spain], Fabrica Pisana [Italy], etc.)
1826	Pilkington (UK) – Bought by NSG Group in 2006
Mid-nineteenth century	Glaverbel (Belgium) created in 1961 by merging of Glaver (founded in 1931) and Univerbel (founded in 1930), through mergings of plants/companies created in the nineteenth century. Bought by Asahi Glass Company in 1981
1848	Boussois SA (France), then Boussois Souchon-Neuvesel in 1966, then BSN in 1967. Bought by PPG Europe in 1982, then by AGC in 1998
1883	PPG (USA)
Late nineteenth century	Detag (Deutsche Tafelglas AG) merged as Flachglas with Delog (Deutsche Libbey Owens Gesellschaft für maschinelle Glasherstellung AG) funded in 1925, then bought by Pilkington in 1980
1907	Asahi Glass Company (AGC, Japan)
1918	NSG Group – Nippon Sheet Glass (Japan)
1951	PFG (South Africa), for a while the only producer of float glass in Africa
1956	China Luoyang Glass Group (China)
1962	SIV-Società Italiana Vetro (Italy), bought by Pilkington in 1995
1964	Taiwan Glass Company (Taiwan)
1965	China Glass Holdings (China)
1970	Glass processor Guardian (founded 1932, USA) entering flat-glass production
1980	Farun (China)
1984	CSG Holding (China)
1986	Muliaglass (Indonesia)
1987	Fuyao (China)
1988	Xinyi (China)
1992	Glass processor Cardinal (founded 1962, USA) entering flat-glass production
1995	Euroglas (Europe), with a first plant built in France

technological innovation, the latest of which was the float revolution. The explanation probably is that process knowledge was not widely disseminated in an industry that was in addition requiring large investments.

After seven years of research and development [6], the float process combined in 1959 the advantages of plate and sheet glass with a quality that quickly became equivalent to that of plate glass at much lower investment and production costs. Over the last 50 years, the process has thus been implemented worldwide, causing an almost total end to sheet-glass production. After its invention, Pilkington decided to license the process to other producers. The first license was signed by PPG on 27 July 1962, quickly followed by Glaverbel, Boussois, Saint-Gobain, Saint Roch and LOF and preceded by Asahi Glass Company, Nippon Sheet Glass, Ford, Mexican Vitro, Sklo Union (Czechoslovakia, at that time) and Bor (Russia). The last company to get a license in the 1960s was Central

Glass, in Japan, in February 1968. By the end of the 1960s, 20 float lines had been built but about 20 plate-glass plants were still operating. Boussois (France), for instance, closed its plant in the late 1970s after completing production of a yellow glass for the Sydney Opera.

Pilkington's policy was "not to create new flat-glass manufacturers" [7]. This is the reason why Pilkington was reluctant to provide licenses to companies that were not already making flat glass, thus excluding Guardian, which was only transforming flat glass at that time. Hence, it was believed in the 1960s that flat glass would remain a business/industry controlled by the Western world, especially because beginning float production by the new licensees could be difficult. As, for instance, reported by the New York Times in 1964, "Robinson F. Barker, vice president of Pittsburgh Plate's glass and fiber group, noted last week that the company's Cumberland float plant is just now emerging from severe start-up

difficulties,” and the Times added that “Setting up float-glass plants may also involve labor difficulties. One company that wanted to convert one of its plants to the float process was blocked by a union that objected to having a number of jobs eliminated, according to an officer of the company.” In the mid-1970s, however, float did take over sheet glass so that by the end of the decade only a few sheet plants were still in operation in North America and in Europe. In Europe, this move during the 1970s indeed caused the elimination of many jobs and, therefore, created social difficulties especially in Belgium, France, and Germany [8].

Barred from access to the technology, Guardian thus stormed into the industry by building in 1970 a factory without holding a license [7]. With the beginning of its first float line in the United States in 1970, it radically changed the landscape of the flat-glass world by focusing on a few standardized products, avoiding not only research and development but also marketing departments, making instead plant managers responsible for production and sales, and not participating in glass-maker associations or in the elaboration of industry standards. In these ways, Guardian forced the whole industry to become a low-cost business. That impact was felt very strongly in Europe, in particular, where Guardian Industries opened its first line in Luxemburg in 1981, which was the first they built abroad.

3.2 The Changing Geography of Float Glass

Until the mid-1980s, the float-glass industry was thus mainly located in Europe, United States, and Japan where the first licensees increased their number of lines. Knowledge and intellectual property, which had been controlled by Pilkington up to the early 1980s during the validity period of the patent has since been widely dispersed among many engineering companies having the capability to design, build, and start up new float lines. These companies have demonstrated the appropriate readiness to support newcomers. From the mid-1980s, they have thus facilitated the entrance of new companies which were coming mainly from the flat-glass fabrication industry, such as Cardinal or Euroglas.

In terms of number of float lines, it is interesting to note the similarities over the years between Western Europe and the United States until the late 1990s. A slight divergence then appeared, preceding the real difference that manifested itself in 2008 when Western Europe had to eliminate excess production capacity and old production sites. At last, an economic crisis marked by a deep recession had made these difficult decisions inevitable. In one respect, however, production has been fortuitously protected from foreign competition by the decision taken in the early days of the float process to produce standard

6.0 × 3.21 m sheets, to which tools have been fitted in the transformation industry. It happens that this *jumbo* size is too large to fit into containers, which are required for economic ship transportation.

In contrast, rapid industrialization in China has resulted in the sustained creation of plants, whose number has increased so quickly that it became higher than in both Europe and United States in 1997 and is now representing more than half of the worldwide total (Figure 1). As might be expected, Chinese companies are selling their glass products on the international market, mainly for automobile replacement, appliances, communication devices, or solar energy. Another significant trend is an analogous increase, but at a lower rate, of the number of float lines in Africa and the Middle East (Figure 2) where competitive advantages are provided by low costs

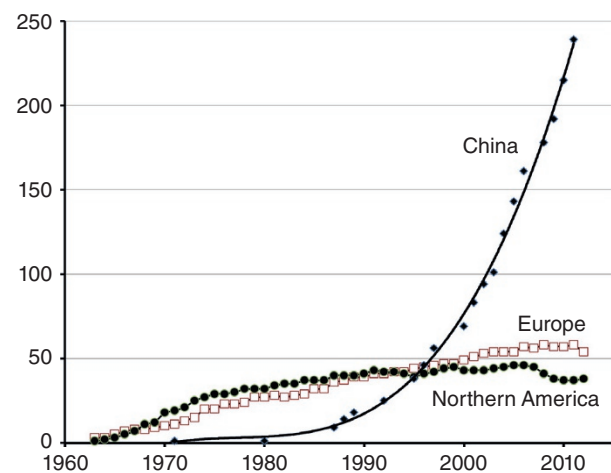


Figure 1 Float lines in Europe, North America, and Middle East/Africa (from 1960s to 2013).

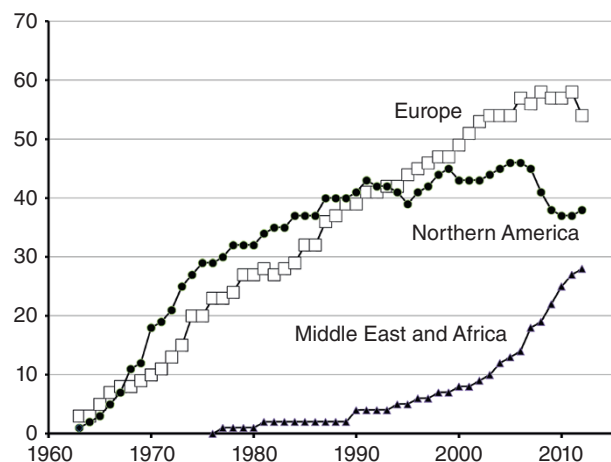


Figure 2 Increases of the number of float lines in Europe, North America, and Middle East/Africa from 1960s to 2013.

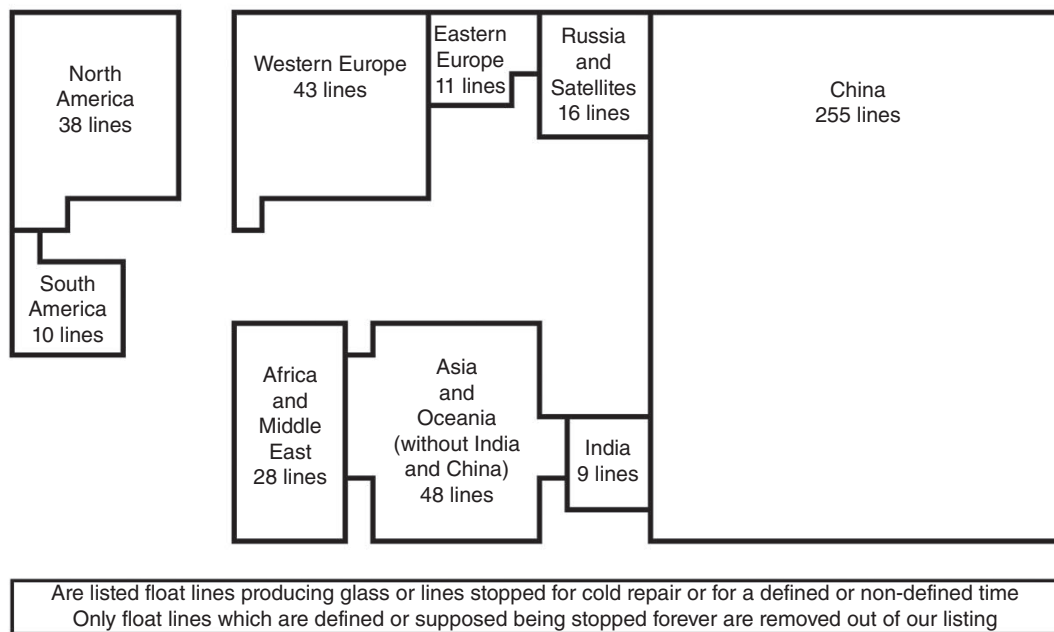


Figure 3 Float lines as of early 2013.

for either energy or manpower. In this respect, exportation of finished products far away the production sites is made possible by low costs of transportation, by boat for long distances.

It is convenient to divide the current flat-glass world into nine regions (Figure 3), namely North America, South America, Western Europe, Eastern Europe, Russia and satellites, the Middle East and Africa, China, India, and the rest of Asia along with the Pacific region. In the Middle East/Africa, South America, and India, float glass has been absent for so long a time that the current development should keep continuing for a while. As an example, the overall flat-glass consumption is about 10 kg per person and per year worldwide, but with high values of 30 kg in several European countries that contrast with only 1 kg in India.

The flat-glass business is dominated by key players but a comparison between the data for 1988 (Table 8) and 2015 (Table 9) shows how deeply has the market changed. During the 1980s, Pilkington and PPG were the main flat-glass companies. Along with Saint-Gobain, they controlled about 40% of the business. Altogether, North America, Western Europe, and Japan had a total of 87 lines that represented 75% of the world production. In 2015, their number of float lines has slightly increased to almost 100, but this higher number barely account for

Table 8 Main producers of float glass in 1988 [9].

Company	Number of float lines	Global market share (%)
Pilkington (with LOF)	15.5	15
PPG	16	13.5
Saint-Gobain	13	13
Asahi (with Glaverbel)	9	8.6
Ford	8	7.2
Guardian	7	6.5
AFG	6	5.7
Nippon Sheet Glass	4	3.6
Central Glass	3	2.8
SIV (Italia)	2.5	2.5
Hankuk (Korea)	2	2.1
Vitro (Mexico)	2	2.1
Sisecam (Turkey)	1	0.9
Taiwan Glass (Taiwan)	1	0.9
Other	~26	
Total	~116	

Table 9 Main producers of float glass in 2015.

Company	Number of float lines	References
NSG Group	46	(1)
Asahi Glass Company (AGC)	37	(2)
Saint-Gobain	36 (nine in partnership)	(3)
Guardian	28	(4)
Kibing (China)	21	(5)
Taiwan Glass (Taiwan/China)	17	(6)
Xinyi (China)	17	(7)
China Glass Holdings (China)	14	(8)
CSG (China)	12	(9)
Jinjing Glass Group (China)	10	(10)
Sisecam (Turkey and Bulgaria)	11	(11)
Fuyao (China)	9	(12)
Other (about 75 producers)	About 250	(13)
Total (in the world)	About 500	(14)

- (1) Management of, or interests in. NSG presentation, 30 April 2015.
(2) AGC 2015 presentation, Reference, May 2015.
(3) 2012 Saint-Gobain Annual report (English version).
(4) Guardian Industry internet website (2015).
(5) Kibing Glass Profile (March 2015).
(6) Evaluated by the author from Taiwan Glass data.
(7) Evaluated by the author from Xinyi data.
(8) China Glass Holdings, 2014 Annual Report.
(9) Evaluated by the author.
(10) Evaluated by the author.
(11) Sisecam presentation, January 2015.
(12) Evaluated by the author from Fuyao data.
(13) Evaluated by the author.
(14) Evaluated by the author.

20% of the world capacity. Especially noteworthy are the facts that Ford completely quit flat-glass production, Pilkington and SIV are now part of NSG Group (Nippon Sheet Glass), Hankuk is integrated into Saint-Gobain, and PPG has strongly streamlined its business by selling all its operations outside North America. Although NSG Group, Asahi Glass Company (AGC), Saint-Gobain, and Guardian Industries are still dominating the business, new companies are becoming global with the potential to modify that hierarchy in the years to come.

3.3 Development and Profitability

After many good years, most flat-glass companies in Europe, North America, and Japan have suffered from a deterioration of their profitability and sales growth, if not from a production decrease. Hence, the 2008 economic crisis took place in a business environment that was already difficult. Some companies have anticipated this new era by strongly reducing their glass activities within their portfolios or even selling them completely. Good examples are BSN, which left totally the glass industry in 2004, and PPG, which was number one in the mid-1980s and later sold its flat-glass business to Mexican Vitro and its fiber-glass operations to Nippon Electric Glass (NEG) in 2017. It has now become a global leader in paints.

In this activity redistribution, an important event has been the purchase of Pilkington by NSG in 2006. Highlighting the strong influence that final users may now exert on flat-glass producers, this purchase was motivated by the need to match the overseas expansion of the Toyota car maker, one of NSG's key customers. Whereas 80% of NSG sales were in Japan before this acquisition, 80% of the sales are now made overseas. But such an increase of the market's share in a context of decreasing prices has been accompanied by a marked drop in stock value as the company's profitability strongly decreased along the way. This situation is not particular to NSG. It has been acknowledged by stock markets around the world, which have strongly devalued their assessment not only of the "pure" flat-glass companies but also of companies having a large portion of their sales in the flat-glass business in the Western world.

The contrast with African, Middle East, Chinese, and other Asian companies is striking since these have in contrast enjoyed at the same time good or even impressive growth of both production and profitability, especially in China. But the extremely strong increase in the number of Chinese plants was of course not sustainable indefinitely (Figure 1). Under governmental pressure, production lines have lately been shut down and companies – including some large ones – have even quit the business to eliminate excess production capacity. By the end of 2017, it was estimated that about only 250 plants were still operating out of a total of more than 340 built. This situation notwithstanding, Chinese flat-glass companies such as Fuyao, Kibing, or Xinyi will likely become global to lead the business and strongly contest the leadership of Western companies along with other companies (like Sisecam in Turkey) that are benefiting from a strong national market.

3.4 Some Flat-glass Economics

In the flat-glass market the deterioration of the profitability has many causes. One of them is the price of glass, which has decreased continuously (in constant currency) during the last 50 years (Figure 4). Improvements in productivity and implementation of business models focused on the low-cost production exemplified by Guardian Industries have intensified price competition all around the world during the last three decades. As a result, there has been a very striking contrast between the price of flat glass in Europe and the United States and standard price indices (e.g. construction and consumer indices in France and the United States, respectively, in Figure 5).

Actually, this trend is the continuation of a long evolution that began with the Industrial Revolution. A pioneering study has, for instance, clearly documented the continuous

decrease of production cost and selling prices of plate glass, window panes, and bottles resulting from the technical advances made between the French Revolution and the late 1980s [10]. In other words, flat-glass products are no longer rare and expensive items made by relatively few producers. They have become commodity articles made by a single process shared by all producers. Although productivity improvements and reduction of specific energy consumption have led to reduction in production costs, the profitability of Western companies has been impacted by the pressure exerted on market prices by foreign low-cost producer whose number has continuously increased, especially from the mid-1980s.

The cost of a flat-glass plant was about 50 million US\$ in the early 1970s [11] or about six times more at constant dollar in 2015. With a much improved technology, the 2014 cost was ranging from 120 to 150 or less than 100 million US\$ depending on whether the engineering was Western or Chinese. Still more striking is the contrast between the original 500 tons typically produced daily by 400 people in the 1970s and the current 800 tons made by fewer than 150 people.

Four key components mainly determine the production costs: raw materials, energy, manpower, and initial investment. Specifically, typical production costs of float glass in the Western world are split into raw materials (20%), energy (21%), labor and overheads (29%), depreciation (10%), transportation (10%), and remaining items (10%). The energy efficiency in glass furnaces can widely differ depending on size and technology and on the amount of cullet used. Along with manpower, however, energy will likely remain the main factor to be taken into account for the location of production sites.

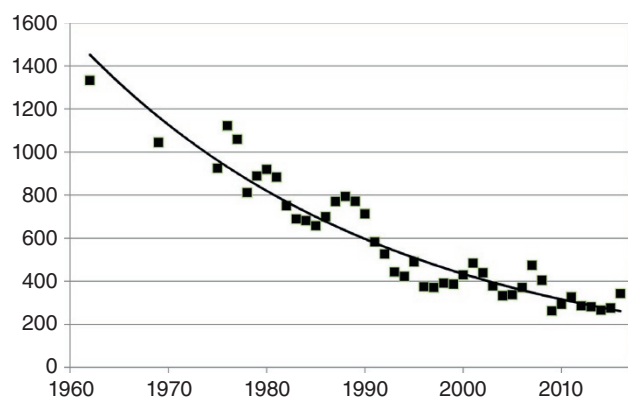


Figure 4 Decrease of the price of clear flat glass in Western Europe from 1960 to 2014 in constant euros per ton.

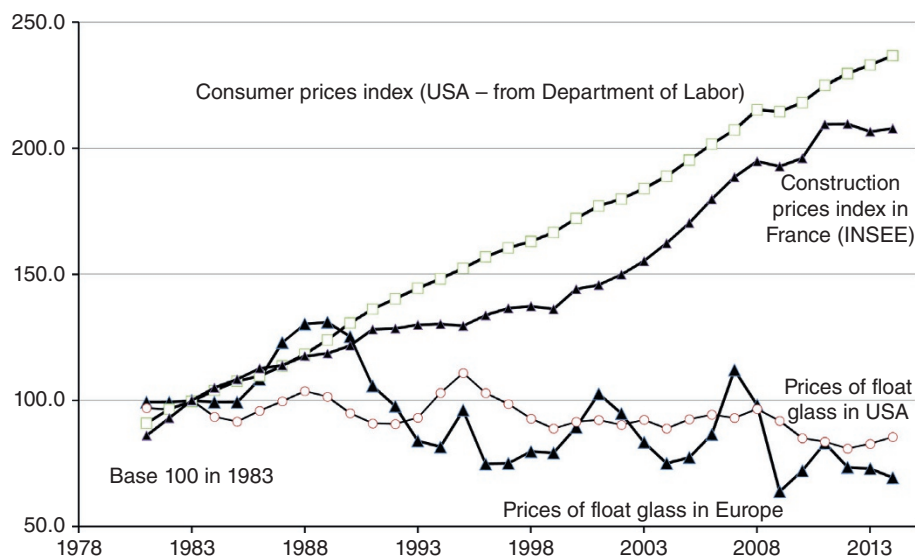


Figure 5 Divergence between the prices of flat glass in Western Europe and in the United States from 1981 to 2014 and the construction price index in Paris (INSEE) and the consumer price index in the United States (Department of Labor).

Float-glass lines, nowadays, are often associated with the first level of transformation. Coatings are the prime example as low-emissivity panels have become mandatory for insulating glass in many countries, but other laminated-glass production lines or mirror production lines. In the long term, we can thus expect that 50% of the flat glass utilized by the building industry will be transformed (at the first level), which is about 40% of a float line output.

3.5 Market Trends

The float process has induced a radical change in the flat-glass industry when it introduced through its breakthrough technology a “dominant design” in the 1960s and 1970s. As already stated, spreading of the technology and know-how from the late 1980s throughout the world has transformed flat glass into a commodity product, whereas low energy and/or manpower costs have promoted a rapid development of the industry in China and the Middle East. Today, more than a dozen engineering companies are able to design, build, and operate a float line, thus offering the capabilities for any new investor to participate in the production. We are thus far from Pilkington’s original concern in the 1960s that float-glass licensing “was not to create new flat-glass manufacturers”!

As of early 2018, float glass is produced by 445 lines (running or in repair) worldwide, whereas about 200 other lines are making cast or sheet glass. A few float lines are producing borosilicate glass, generally with a tonnage lower than 100 tons per day. Most of the products sold today are either clear glass of 2–25 mm thickness or coated low-emissivity glass. But the absence of new products sold in large quantities has trapped during the last 10–15 years the industry in a spiral of low-price competition, which has much reduced the profitability of most companies located in Western world.

At the same time flat-glass secondary fabrication has been strongly modified by coatings, tempered and laminated safety products, and industrialization of insulating glass. But producers of equipment and machinery (most of them located in Europe) and some glass industry suppliers (such as logistics and transportation companies) have also been strongly impacted by the capabilities of Chinese or Asian newcomers. Several Asian suppliers or Western companies located in Asia (or producing a large portion of their equipment in Asia) are currently leading the market.

As a result, successful companies have largely left the flat-glass business when they have not just remained in some profitable niche markets such as extra-thin or electrochromic glass, or developed production outside the Western world. Another noteworthy feature is that flat glass is no longer a business almost exclusively focusing

on the building sector. Whereas the growing photovoltaic industry requires patterned products, the electronic business is requesting extra-thin glass for semiconductor substrates, touch panel displays, or fingerprint sensors (Chapter 6.10), which is made with either the float or down-draw process (Chapter 1.4). In both cases, the market is expected to grow much faster than for more traditional products.

4 Perspectives

In the early 1960s, the flat-glass industry was driven by glass producers, mainly located in developed countries. These had the required knowledge, which gave them an edge over the fabricators to which they were selling the primary material that they were not transforming themselves. Today, flat-glass production knowledge has been widely dispersed whereas the complexity with which flat glass is used in many applications also requires such a technological know-how that has made processors, façade and window companies, and flat-glass customers, in general, more powerful than glass producers.

In this context, noticeable price increases are not to be expected in an industry that remains fragmented with almost 100 producers. If South America and India should be very active markets in years to come, the situation remains uncertain in Africa and Russia whereas consolidation is expected in some regions. This is especially the case of Western Europe where the “jumbo strategy” cannot prevent large quantities of flat glass from being imported as finished fabricated products for which long-distance transportation is not much of an issue. Under these circumstances, the number of producers should not increase. Rather, one should expect a restructuring induced by the pressure exerted by extra-European producers. By comparison, the US flat-glass industry should be less strained, thanks to the lower energy costs it is now benefiting, thanks to shale gas.

Over the last 50 years [12–16], the flat-glass business has faced two major situations that were not anticipated by the inventors of float glass: a move of the production leadership out of the Western world to Asia, South America, or the Middle East, and another move of leadership – and added value – for product and process development from the glass producers to many other stakeholders involved in engineering, design, fabrication, glazing, or supply.

Most of the flat-glass products are very mature. Float glass (and most of the fabricated products) is nowadays a commodity. Market niches are very small but can remain profitable enough for companies able to exploit properly these areas. In other words, the flat-glass

industry needs new breakthrough innovations – its fifth revolution – to revive a sustainable profitability. The melting process, which is old and needs to be improved could be its target, which is why active research is being made in this field by glass companies. The current business model needs also revolution to renovate flat-glass industry practices.

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9.7

Design and Operation of Glass Furnaces

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1 Introduction

To a large extent, the history of glassmaking is that of melting furnaces. Throughout the ages, the course of the reactions between the raw materials largely determined quality as well as production volumes and cost. Thanks to the new science of thermodynamics, the major improvements progressively brought in the nineteenth century resulted in the invention of the *regenerative tank* furnace (Chapter 10.9). Not only were then melting temperatures higher and more uniform, but heat hitherto wasted was recovered while continuous instead of batch melting ensured the much higher throughputs, more durable equipment, and lower labor costs that have since then sustained the expansion of the glass industry.

Modern furnaces are typically from 8 to 40 m long, 5–15 m wide, and hold enough glass over typical depths of 0.9–1.4 m to ensure a daily production ranging from 20 to 700 tons with extreme pulls exceeding 1000 tons for a total investment cost ranging from about 2 to 15 M€ as of 2019. These furnaces of course differ from those designed by the Siemens brothers and other nineteenth-century engineers, but the basic goals involved have remained the same, namely to save as much energy as possible and to deliver continuously at the best cost a homogeneous melt ready to be shaped. The main changes have been: (i) the switch from coal to natural gas, heavy oil, or electricity as a heating source; (ii) the nature of the refractories used for the tank, combustion space, and preheating chambers [1], which have much benefited from advances in the technology of ceramics and other relevant materials; (iii) the precise tailoring of a furnace in terms of the energy sources available, targeted pull rate

(and possibly intended variations), kind of production and raw materials used, cullet included (Chapter 9.9); (iv) the manner in which the geometry of the tank and its temperature distribution are designed to optimize melt homogenization and fining by the currents generated by the free convection caused by temperature and density differences, the exerted pull, and possible bubbling and electrical boosting; (v) and increasingly strict environmental regulations in terms of emissions of CO₂ and pollutants, particular emphasis being put on sulfur and especially nitrogen oxides (SO₂, SO₃, NO, NO₂, N₂O, and their derivatives), which are generically denoted by SO_x and NO_x, respectively.

Like in any complex industrial production, changes in the various chemical and physical factors involved may have opposing effects in the technical optimization of the overall process as well as on fabrication costs. Compromises have thus to be found, which is why a given furnace will be adequate for a given use at some place but not for others elsewhere. This is also why a new furnace still requires much experience from its designer in spite of the wealth of information that can now gathered a priori from computer simulations of the whole melting operations (Chapters 1.7 and 9.8).

To review these various features in this chapter, a brief overview of furnaces will first be provided through their *hearts* (the melters) and *lungs* (the regenerators) and of the five main types of heating systems. The fusion process itself will not be addressed because it has already been described in Chapter 1.3. A more detailed description of the tank and superstructure of melters, of the regenerators, and of their ancillary equipment will then be given, interest being paid to the nature of the refractory materials used whose resistance to corrosion and thermal shock are critical in any respect [2]. Finally, some general considerations about furnace design will be reviewed before the issue of pollutants emitted such as NO_x will also be

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considered in view of the ever stricter nature of environmental regulations.

In contrast to forming processes, which are mainly determined by the kind of production (e.g. float process for window glass), melting of the batch can be made with different types of furnaces for the same production. More than elsewhere in the Encyclopedia, economic factors will thus form the backdrop to the present chapter. From this standpoint, a basic figure is the specific load, which is the amount of glass daily produced by surface area of the melter: the production (in tons per day, tpd) is then derived at once from it and the melter surface. As illustrated by the fact that melting alone represents 60–70% of the overall energy spent in glass production [3], the energy efficiency is another fundamental notion to which another chapter is devoted (Chapter 9.8). In view of the introductory nature of the present account, interested readers are referred to standard treatises for more detailed descriptions (e.g. [4]).

2 The Furnace Families

2.1 Common Features

Glassmaking furnaces are generally not specific to a given type of production because their operations depend on so many factors that they can be optimized in different ways and adapted to particular features of the glass produced (e.g. fluor volatilization in opal glass, low thermal expansion of borosilicates, high Fe content of rock wool). In contrast, their sizes depend on the subsequent forming process because they are mainly determined by the desired pull rate. This is the obvious reason why the biggest are those designed and built for float glass (Chapter 1.4).

The most conspicuous part of a furnace is the melting tank (Figure 1). It is fed with the raw materials coming from the outside batch silo at the *doghouse* whose design depends on furnace type. The batch is heated up to typically 1500 °C at the *melting end* on one side of the tank, which can include a dam wall as well as bubbling and electrical-boosting systems to achieve complete melting. Sometimes in a *refining bank* that is shallower and hotter than the other parts of the melter, the distinct steps of primary and secondary fining then follow to yield a chemically homogeneous melt bearing as few defects as possible at the *working end* on the opposite side of the tank (Chapter 1.3). There, the melt is delivered through the *waist* (or *neck*) for float glass (Chapter 1.4), the *throat* for container glass (Chapter 1.5), or by overflow for rock wool (Chapter 9.13). Depending on the kind of furnace used, the melt is then *conditioned* on its way to the forming devices so as to reach the appropriate homogeneous

temperatures and viscosities required by the process. To achieve the temperature reduction of 150 °C for example needed for container production, the glass is cooled at the center of the feeder canal but need to be heated at the sides where cooling would be too fast.

The volume of the space left above the tank up to the *crown* depends on the heating system, being small for electric melting but large to accommodate the burners of a combustion chamber. Whenever flue gases are produced, furnaces include either *regenerators* or *recuperators*, which are of the same types as those used in other high-temperature processes [3]. As originally designed in the nineteenth century, regenerators transfer discontinuously heat that would be lost to the chimney to the combustion gases before they reach the burners (Chapter 10.9). They consist of two or of an even number of chambers designed to store as much heat as possible in a checkwork of refractory bricks (a *checker*, for short). In one chamber, the flue gas typically cools from 1450 to 600–400 °C while the combustion air may heat up to a maximum temperature of typically 1100–1300 °C in the other chamber; the additional heat thus delivered to the combustion space increases the heat set free in the furnace beyond the level reached by the net calorific value of the fuel alone (Chapter 9.8). Every 20–30 minutes, depending on the *thermal load* of the furnace, the flows of both fluids alternate in less than one minute during which firing stops. With recuperators, heat is in contrast exchanged continuously between the flue gas and combustion air through a co- or counter-current. What then matters is not the capacity of the exchange medium to store heat but to transport it rapidly. These devices are often termed *radiative* recuperators because of the nature of heat transfer from the hot flue gas; the colder combustion air is in contrast heated up by convection only, up to 750 °C with the most efficient systems. Thin-walled materials are required for the exchange. For mechanical reasons, high-temperature steels must be selected but they severely limit the entry temperatures of the flue gas. Although recuperators are theoretically more efficient than regenerators, they do not reach the efficiencies of regenerators in glass furnaces.

Sometimes with the help of electrical boosters, the batch is most frequently melted by the heat radiated directly by the flames (adiabatic temperatures of about 2700 and 3000 °C for air-fuel and oxy-fuel combustion, respectively; technical temperatures of 1650–1800 °C for both cases) and indirectly by the crown at typically 1600 °C (Chapter 9.8). Since the 1960s, burners are fueled with natural gas (methane, CH₄) or preheated heavy oil atomized in a nozzle by means of pressure or compressed air or methane. Solid fuels are mainly used in China where petcoke, a residue from petrochemistry, is transported to burners by means of propellant air.

2.2 End-Fired Regenerative Furnaces

Because they are economically efficient for various kinds of production (Table 1), end-fired furnaces are at present the most common. They have two ports equipped with 2–4 burners each and located on a single side next to the regenerator (Figure 1a). The flames from one port develop over the whole length of the furnace and turn 180° back toward the other port where the flue gas is extracted. This U shape gives them a long residence time. Their advantages are a highly preheated combustion air and a relatively low energy consumption. As a result, they have a high thermal and overall energy utilization efficiency, which translates into a high production efficiency and a high specific load. Owing to this efficiency, they are becoming extensively used to produce container glass. As a disadvantage, they allow for a limited control of energy distribution along the longitudinal axis of the furnace, which results in some limitations to achieve an ultimately high glass quality. Their investments costs are relatively high, however, as are their NO_x emissions, and they require maintenance work for chamber cleaning and fixing expansion joint areas for furnaces larger than 10 m.

2.3 Cross-Fired Regenerative Furnaces

By far the biggest ones, cross-fired furnaces are mostly dedicated to float glass (Table 1). From 4 to 8 burner ports are placed on two opposite sides next to the regenerators (Figure 1b), so that the temperature profiles along the longitudinal axis of the furnace can be tuned to obtain for primary fining a hot spot of a given size at the right place. This results in an enhanced control of glass quality, an important issue since the presence of a single tiny seed may lead to the rejection of a large flat glass sheet. Cross-fired regenerative furnaces are less energy efficient and reach lower specific loads than end-fired furnaces. The arrangement of the regenerators makes them more

expensive to build. And a latent problem in float furnaces is the clogging of the first chamber sections of their regenerators by the dust carried by the flue gas.

2.4 Recuperative Furnaces

Float glass is the main product not melted in the other kinds of furnaces (Table 2). In *recuperative* furnaces (Figure 2a), firing has the advantage to be continuous. From 5 to 15 burners are placed on both sides so that temperature profiles can be tuned finely. Other advantages are low NO_x emissions for container glass, a clean combustion air, and low investment costs due to relatively low air preheating, with the resulting disadvantage of high energy consumption and, thus, of lower furnace efficiency.

2.5 Oxyfuel Furnaces

Dating from the 1990s, oxyfuel furnaces (Figure 2b) are recent developments. The oxygen content of the combustion gas is increased to 91–98 vol % to avoid the energy wasted for heating the 78% nitrogen (and 1% argon) of the air up to the combustion temperature and reducing at the same time NO_x emissions and the volume of flue gas produced. The oxygen is generated on site either cryogenically or via pressure swing absorption by zeolite molecular sieves or, alternatively, is delivered as a liquid in tanks or by a pipeline from the production site. The efficiency is much higher for oxyfuel than for other fired furnaces so that the specific load is also higher. A very good adjustment of the temperature profile over the furnace axis is again possible, but condensates are generated by the wet waste gases. Oxygen generation not only means very high operating costs, however, but often difficulties for suppliers to backup the availability of liquid oxygen beyond a certain tonnage. In Europe and most parts of the world, oxyfuel furnaces are profitable only if electricity costs are less than

Table 1 End- and cross-fired regenerative furnaces.

Glass type	Size (m ²)	Yield (t/d)	NO _x ^a (mg/Nm ³)	Size (m ²)	Yield (t/d)	NO _x ^a (mg/Nm ³)
	<i>End-fired</i>			<i>Cross-fired^b</i>		
Tableware	10–160	20–300	950–1500	25–150	30–280	
Borosilicate	15–50	15–60		20–60	20–60	
Ornamental	20–130	50–260		30–120	50–260	
Container	25–225	50–800	550–750 ^c	30–210	50–750	
Float	250–450	375–600		205–850	250–1100	1200–1500 ^c

^a 1 Nm³ (normal cubic meter) = amount of gas in a volume of 1 m³ at 273 K and 1 atm; values relating to 8% remaining oxygen and dry flue gas, which depend on the type of refining system.

^b For 2-burner systems; 700–1000 mg/Nm³ for 3; and up to 2000 mg/Nm³ for special glasses.

^c 550–750 mg/Nm³ with heavy oil, 700–1000 mg/Nm³ with natural gas.

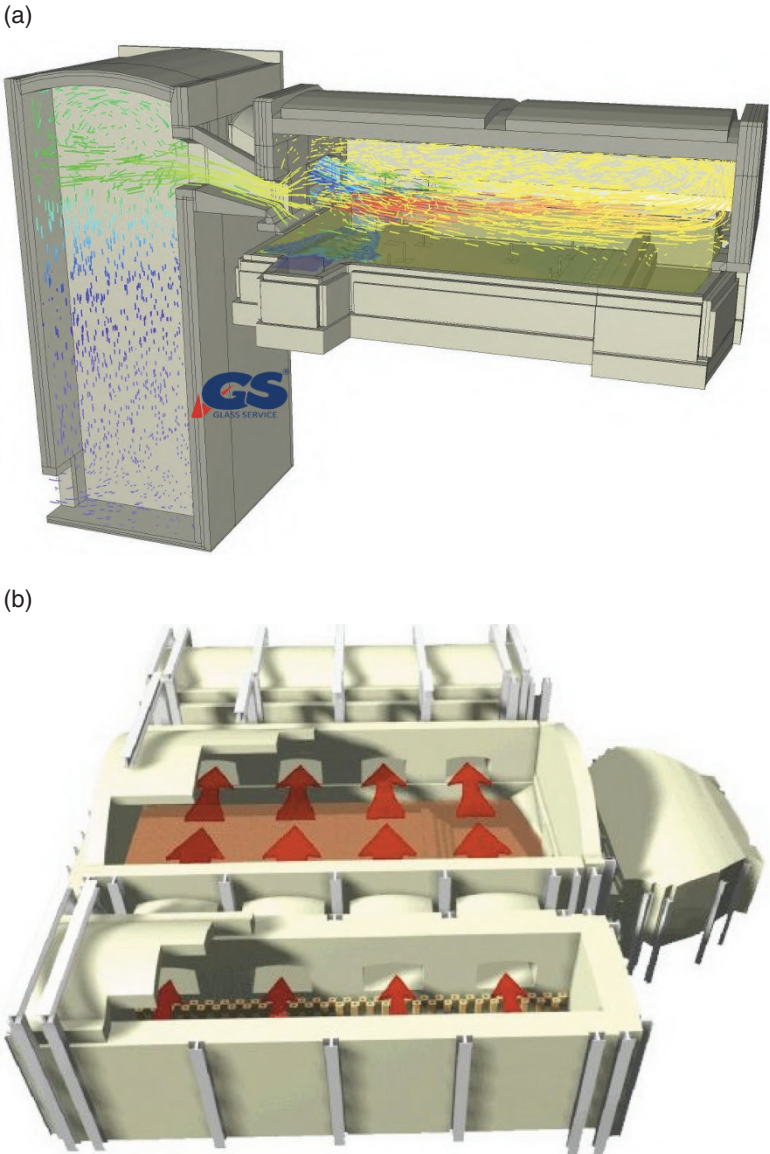


Figure 1 Regenerative fired furnaces for container glass. (a) End-fired, standing against its regenerator; hot flue gas of the U-shaped flame penetrating in one chamber to be cooled downward, combustion air coming up from the other chamber. *Source:* Sketch courtesy Glass Service. (b) Cross-fired, in between its two long regenerators. *Source:* Sketch courtesy Horn Industries AG.

Table 2 Summary of other furnaces.

Glass type	Size (m ²)	Yield (t/d)	Size (m ²)	Yield (t/d)	Size (m ²)	Yield (t/d)
	<i>Recuperative</i>		<i>All oxyfuel</i>		<i>All electric^a</i>	
Tableware	15–80	20–140	15–100	40–240	3–30	6–100
Ornamental	30–130	40–260	60–100	80–250	15–30	30–70 ^a
Container	30–175	50–500	70–160	150–600	30–90	0–200
Special	15–50	15–60	4–50	6–60	1–5	
Other	3–15	5–15 ^b	35–100	50–250 ^c	30–50	50–150 ^d

^a Opale glass.
^b Lead-crystal glass.
^c Fiber glass.
^d C and E glass (Chapter 1.6).

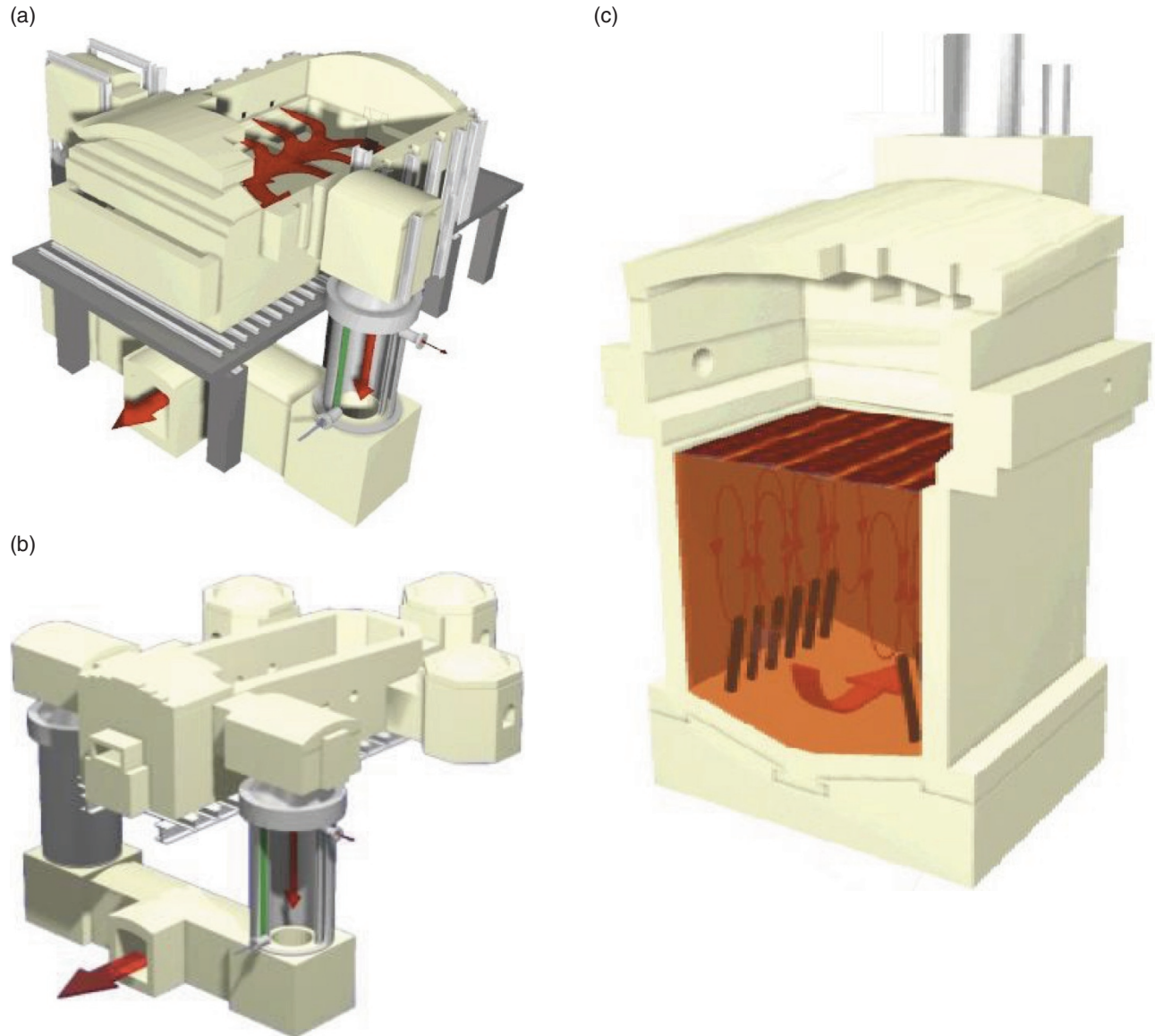


Figure 2 Specimens of other types of furnaces. (a) Recuperative furnace for container glass, with its tall vertical recuperator; (b) recuperative furnace for lead crystal glass; (c) all-electric-melter for tableware glass. *Source:* Sketches courtesy Horn Industries AG.

0.035 €/kWh (2018 value). They are nonetheless drawing more interest for environmental reasons especially in the United States. An interesting development has been brought to the market by Praxair Co. with the OPTI-MELT™ system, which uses a regenerator for preheating a mixture of flue and natural gases to produce a synthetic gas that is then fired with oxygen. By this process, part of the thermal energy of the waste gas is converted into chemical energy to enhance efficiency.

Oxyfuel furnaces are by definition especially advantageous if higher melting temperatures are required (e.g. for cover glass above 1700 °C) and for the production

of glass of a very high quality. Cases in point are continuous fibers for which even microscale defects (i.e. inclusions or local composition variations) cause breakage of the thread in the drawing machine. To ensure excellent quality, however, boosting and/or bubbling systems as well as different wall types and even a refining bank can be needed. When float glass is made with two production lines, an all-oxyfuel furnace also makes sense because the waste nitrogen is recycled in the atmosphere of the two tin baths (Chapter 1.4) while energy consumption with 100% oxygen may be reduced by 25 % and emissions of CO₂, SO₂, and NO_x by 15, 38, and 83 %, respectively.

2.6 All-Electric Furnaces

As indicated by their names, all-electric furnaces (Figure 2c) melt the batch with intense electric currents delivered by arrays of electrodes immersed in the molten glass [5–7]. Earlier, electrodes were made of graphite but they suffered from short operation times of 1–5 months and current densities of 0.3 A/cm² only. Today, currents of typically 200 V and 4000 A per array are most frequently delivered by electrodes made of molybdenum, which stands out by its high melting point of about 2600 °C and its high thermal-shock resistance ensured by a low thermal expansion but gets highly corroded under strongly oxidizing conditions. Molybdenum is available in diameters from 30 to 150 mm and lengths up to 2.5 m. The electrodes are operated at voltages of 200 V, 50 Hz AC, and reach current densities of about 1.5 A/cm² corresponding to currents of 1–3 kA per electrode array.

For high-purity optical glasses, Pt or Pt-Rh electrodes are used at current densities of up to 2 A/cm². They have excellent corrosion stability in oxidizing melts but are sensitive to reducing conditions and must be operated at AC frequencies of typically 1–10 kHz below which metal dispersion into the melt would take place. Other electrode materials like SnO₂ (0.5–0.7 A/cm²), W, or MoZr₂ are used in special cases only.

Electrodes are also widely used for additional energy input in fossil fuel-fired furnaces. This is obviously advantageous in terms of NO_x emissions. For container glass, however, fully electric melting of colored glass is not possible when strong ion absorption in the infrared (Chapter 6.1) makes heat transfer inefficient within the bath. Very expensive backup systems for uninterruptible power supply are in addition needed and the efficiency loss caused by high-voltage lines from the power station is often not considered, which is to be viewed critically from an environmental standpoint.

3 Melter

3.1 Alumina–Zirconia–Silica Refractories

The lifetime of a furnace is determined by the wear of its refractories. A major advance in furnace design thus resulted from the invention of electrofused cast alumina–silica materials in the 1920s (Chapter 10.9), which are highly refractory and have a porosity as low as 1–2% to reduce the interface reaction with the melt to a maximum extent. In addition, the material must have good mechanical properties at the working temperatures and be in particular resistant to thermal shock. Nowadays these constraints are best satisfied with electrofused

alumina–zirconia–silica (AZS) where the ZrO₂ component ensures a unique combination of strength, fracture toughness, high ionic conductivity, and low thermal conductivity [8]. In glass melting, zirconia is also important because of its low reactivity with silicates and the high temperature of 1800 °C of the eutectic of the system Al₂O₃–ZrO₂–SiO₂. Commercial compositions are typically close to that of this eutectic with about 40 wt % Al₂O₃, 40 % ZrO₂, and 20 % SiO₂.

It was initially thought that lower ZrO₂ contents would be preferable because of the stresses induced by the volume changes of the monoclinic–tetragonal phase transition of ZrO₂ at 1000–1200 °C on heating and 1000–800 °C on cooling [8]. The opposite has found to be true, however, because the microstructure of these refractories is the key to their properties. Upon cooling of the electrofused melt, baddeleyite (ZrO₂) usually forms first but eutectic precipitation rapidly takes place in the form of closely entangled skeletal zirconia and corundum (Al₂O₃) laths. These find themselves embedded in 10–20 vol % of a Zr-bearing aluminosilicate glass [1, 9], which is soft enough at the temperatures of the zirconia phase transition to accommodate the stresses it produces. The baddeleyite crystals have a morphology that makes it difficult to expel them from the material upon corrosion and, on the contrary, help to keep the corrosion products in place. Upon fabrication, elements like sodium are added as fluxes whereas oxygen is bubbled through the AZS melt to oxidize any carbon from the electrodes and other species that could react with the molten glass.

The corrosion rate of ASZ does depend on composition, however, being much faster for calcium aluminosilicates than for soda-lime silicates [10]. In the latter case, corrosion begins by sodium diffusion into the amorphous phase of the refractory [9], first causing corundum dissolution and, in contrast, baddeleyite growth due to Zr oversaturation of the newly alkali-enriched phase [11]. At the same time that the microstructure of the refractory keeps degraded in the bulk by other phase changes, the sodium aluminosilicate phase exudes at the surface, leaving cavities at the waterline of the tank that are enlarged by the mechanical wear of the moving molten batch [12]. The corrosion rates are lower for larger checker volumes and they also depend on the sizes of the furnace and melting area, cullet fraction, specific load, boosting, and numbers of job changes. The yearly wear rate typically ranges from 1 to 3 %, but examples of 120 m² furnaces associated with large regenerators of 3.3 m³/m² show that rates as low as about 0.4 % during the first three years of operation can be achieved for 5 % boosting and a cullet fraction of about 20 %. The rates of 0.8–1.1 % observed during the following eight years confirmed that slightly higher investment costs do pay off.

For melting C and E glass (Chapter 1.6), basalt (Chapter 9.3), and other special glasses, Cr-based refractories are alternatively used. With a melting point of 2435 °C, Cr_2O_3 is significantly more resistant to corrosion in silicate glasses than AZS but is much more expensive. Whereas AZS costs from 4000 €/t for bottoms and 8000 €/t for walls and throats, respectively, the price of isostatically pressed chromium oxide is 30,000 and 40,000 €/t for palisades and throats, respectively.

3.2 Tank

The melter is divided into the tank in contact with the glass and the superstructure. In the former, the depth of the glass generally ranges from 900 to 1400 mm (Table 3). The melting and refining ends may be separated by a single- or double-row *dam* or *weir wall* to let the colder glass rise from the bottom for being heated and fined (Figure 3). By enhancing convection and avoiding shortcuts in the flow, one increases output, ensures the required quality, or improves production flexibility and energy consumption. Such a dam can be made of 41% ZrO_2 AZS or of a dense Cr-based refractory and

may need to firmly “anchored” in the furnace bottom by a specially shaped block.

The bottom of the tank consists of refractory layers whose number, nature, and thicknesses are determined by the operating conditions. It typically consists of five layers with different functions.

The first upper two layers make up the *paving*. These are plates of fuse-cast ASZ or, for very corrosive melts without specific requirement for glass color, Al_2O_3 – Cr_2O_3 plates of about 120 mm thickness paved in offset stacking (i.e. such that the joints of the lower layer are covered by the upper plates). It is of utmost importance that no bubbles are generated at the brick-melt interface. Below the paving, a layer of zircon ramming mass, about 80 mm thick, absorbs the tensions caused by the thermal expansion of the paving during heating-up. It also effectively stops any metal drops and small amounts of glass melt that locally penetrate the paving. The mechanical support is secured by the forth layer (200 mm) made of material from the sillimanite (Al_2SiO_5) family. This layer has to carry the load of the glass melt and the upper refractory layers, which amount to 3.5–4.5 t/m² depending on the depth of the glass bath or even 8 t/m² for a deep fining zone. It is directly connected to the steel framework supporting the entire construction. The fifth layer is made of light chamotte bricks. Its function is the thermal insulation of the bottom; its thickness is chosen according to the desired function.

Because the refining end can be as deep as 2800 mm for color container-glass furnaces, its design must prevent the melting part from pushing toward the throat whereas bottom electrodes may be installed next to and also often in front of the throat. The bottom refractories of the refining end are usually the same as those of the melting part, but some layers can be omitted to comply with building requirements or to increase heat losses for glass preconditioning. The entire melting and refining parts are edged by a basin consisting of a combination of 200–300 mm

Table 3 Bath depths: typical ranges and [in brackets] extreme values (mm).^a

Tableware	900–1300 [1400]
Container glass ^a	
Standard green	900–1400 [1700]
Flint	1100–1600 [1700]
Amber	1000–1500 [1600]
Special	750–1000 [1200]
Float	1100–1500

^a Depths of up to 2800 mm in the refining end.

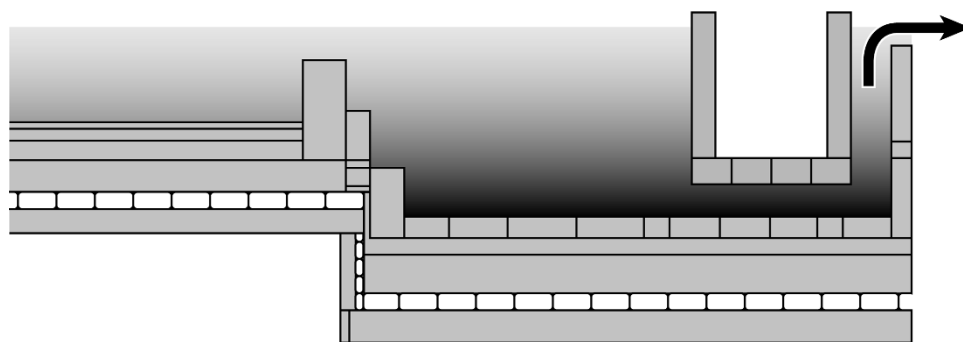


Figure 3 Sketch of a dam wall in the melter of a glass furnace.

thick soldier blocks, arranged without any mortar, between which empty spaces of about 2 mm must be left to let the blocks become tightly packed at 1550 °C through thermal expansion. To account for thermal expansion mismatch between layers, a special arrangement of steel bracing allow all bottoms layers, the wall and the palisades to be loosened upon heating up while ensuring that no joints remain open.

3.3 Additional Tools: Bubblers and Boosters

For colored glass, a dam can lead in front of the wall to *dead* areas without flow so that the effective bath volume is reduced. For sustaining flow in the entire volume of the melting end, a first means is to blow from the bottom large bubbles of air, oxygen, or nitrogen at a certain distance before the dam wall through a specific number of nozzles made of MoSi₂ or ceramics (sometimes sheathed with a Pt alloy), which may be water-cooled to be protected from corrosion. One then increases the specific load of the furnace by causing colder melt present at the bottom to rise toward the surface through local convection currents created around the paths of the bubbles, but at the price of an increased energy consumption.

Depending on color and cullet fraction, bottom electrode blocks are in addition often displayed according to well-defined patterns in numbers that depend on furnace size and required output. The initial bottom and the soldier blocks of the melting end can be specially shaped to enable the installation of such bubbling or boosting systems at a later stage. Boosting can be permanent or required only for certain tonnages in ways that depend on bath depth and electrode arrangement. It has obviously an important impact on the energy efficiency of the furnace. The maximum specific electrical energy to be applied to avoid premature corrosion in a bottom-boosting system is known empirically. For container glass, intensities of 1.5 A/cm² are briefly exceeded in some cases whereas the maximum is 0.8 A/cm² with molybdenum electrodes for other glass types. Depending on size, there may be several electrical circuits. Some 175 m² end-fired furnaces designed for the Indian market have, for example, an installed boosting capacity of about 6 MW, divided into four different circuits.

3.4 Superstructure

The superstructure of the melting furnace consists of walls (port gable, breast, and throat) capped with the crown. The walls have peep holes for inspection of the melting end (Figure 4) and openings to measure the furnace pressure as well as the temperature of the inner crown with lateral optical thermocouples. Likewise, the



Figure 4 A view over a wool-glass bath through the peep hole of the melter. Source: Photo Isover Saint-Gobain, courtesy Jean-Luc Bernard.

flame and the batch distribution are inspected with a camera – or two, for the large float furnaces – installed in the throat gable, which could be combined with an infrared unit for additional temperature measurements.

Nowadays, the superstructure is mechanically independent of the glass-contact section, thanks to the *tuckstone* on which its walls rest, whose weight is exerted on the steel bracing support. A 40 mm joint filled with fiber wool separates the tuckstone nose from the soldier blocks, which can thus freely expand upon heating before being shut closed manually from the outside by a ramming mass or metal oxide–metal welding. Fused-cast AZS bricks backed up by high-alumina refractory layers of the required thicknesses are used to obtain an appropriate temperature profile within the walls. For parts in contact with flames, ceramic-bonded AZS bricks make it possible to use 2 × 1 m ZEBRA™ blocks and to prevent the so-called glassy phase from being exuded and causing glass defects.

As for the crown, it is either freely suspended or rests directly on the side walls with which joints have to be sealed after heating but before tank filling. Depending on the total length, it is split into segments about 4000 mm long. It is made of mullite (3Al₂O₃·2SiO₂) layers, or of AZS for certain glass types, which is most generally lined with silica, especially of a “lime-free” kind to sustain temperatures as high as about 1640 °C. Thermocouples are installed either directly or indirectly. It is because they always represent a weak point over the service life that the aforementioned optical means are paid much interest.

3.5 Operating Features

3.5.1 Batch Loading

As far as possible any contact between the various refractories of the melter and the reactive batch should be avoided to prevent premature damage. For float glass furnaces, pusher-type planar chargers are used to supply the batch as a carpet onto the bath. For container glass, batch piles are often pushed into the furnace by tappets that can forward the batch either horizontally or at different angles. But the most common type of chargers is a chute whose vibration intensity determines how much batch and cullet are supplied. Water-cooled paddles are often installed as an oscillating system in front of such vibrating chutes, which plunge into the glass bath and thus divide the batch into piles that melt much more easily. If the upper part of the charger can be pivoted, then the batch can be directed toward the furnace, which is essential not only for end-fired furnaces having a single doghouse, but also for elongated furnaces (length-width ratio >1.75) with a load higher than 3.3 t/d.m^2 . If the batch piles cannot be divided in distinct parts, *crocodiles* form as snake-like batch piles that melt very slowly and mostly settle on the opposite furnace side, causing high corrosion in the flux line area. Such an irregular settling of the batch translates into unstable temperatures in the superstructure and can influence NO_x values. Screw chargers are also used, but for special glasses for which they “only” deposit the batch onto the surface. An advantage is to allow for tight sealing of the doghouse, but batch materials must not abrade the screw to avoid defects and discoloration especially in low-iron and special glasses.

3.5.2 Monitoring

Measuring and control technologies are of vital importance for running furnaces. The furnace pressure must be monitored near the glass bath to limit (i) any flame

influence, which could cause spurious signal perturbations, and then improper pressure regulation; (ii) glass-level fluctuations and in the end production losses due to weight fluctuations of the gob especially with high-output IS machines for lightweight container glass (Chapter 1.5). The glass level in the tank and partial pressures of O_2 , CO , etc., are also monitored.

Temperatures must also be continuously measured with thermocouples in the regenerator section, furnace superstructure, and glass contact zone for ensuring production stability in every respect. Two different process-control systems are in fact used. The most straightforward would be to regulate the fuel consumption to make sure that the temperature measured at a given place remains equal to the set point appropriate to the batch composition. Because thermocouples age with time, however, the refractories could be massively damaged and the crown totally damaged if a spurious temperature drift were not detected. In the second process, therefore, one rather checks the fuel consumption and considers the temperatures measured in the superstructure only as indicators. In both cases, however, it is very helpful to make detailed pyrometric measurements to detect possible thermocouple aging and to use reliable “EXPERT” systems to compile and analyze continuously all measurements to identify any problem and fix it immediately for stabilizing the production process.

4 Heat Management

4.1 Burners

The design and arrangement of burners are really important issues. To control both flame size and shape, burners are equipped with an inner and an outer nozzle fed

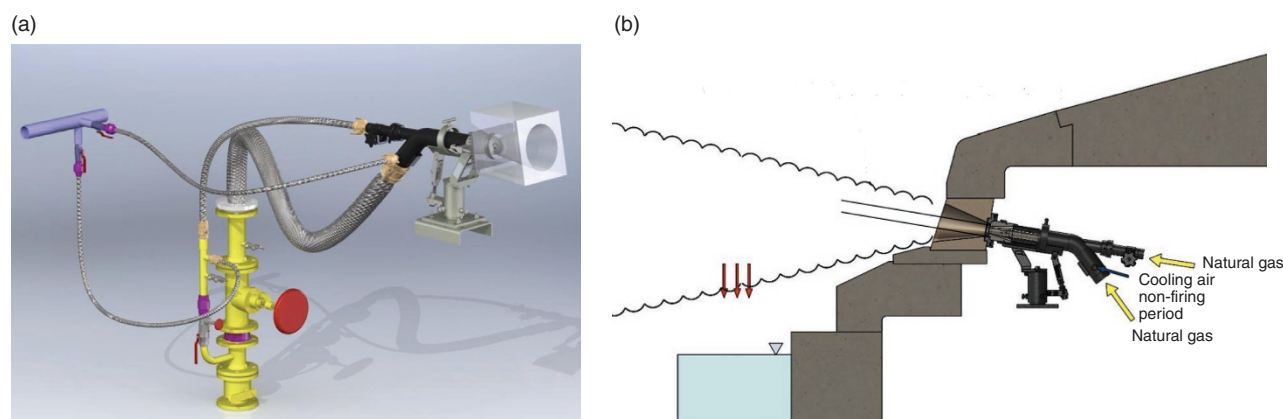


Figure 5 The two nozzle of gas burners (a) and the resulting gas flow (b). Source: Courtesy FlammaTec

by main and secondary fuel gas streams, respectively (Figure 5). In a simple design, the incoming gas stream is divided manually by means of a valve directly attached to the burner. With a more advanced, but expensive method of fuel regulation, the relative positions of both nozzles can be varied, too, to produce very specific flame geometries for primary NO_x control. To stabilize the flames or reduce pollutant emissions, other tools can be installed in the superstructures of the melter. These include oxy-enrichment of the combustion air by pure oxygen, combustion with staged burners, and systems such as ggENOX™, which oppose the flow of flue gas to increase its recirculation and, thus, its residence time.

4.2 Regenerators

The refractories of the regenerators are a driver of the overall investment costs because they represent about 70 % of the total mass of a furnace. As illustrated by an end-fired regenerative furnace (Figure 6), so many parts should be considered for a detailed description of a regenerator that only a few essential elements will be mentioned here. Most important in this respect is the *port neck*, which connects the regenerator to the melter. On the one hand, the differential expansion, especially vertically, of the regenerator and melting end must be adjusted so as to avoid any unintentional shift and keep the expansion joints in the entire sections

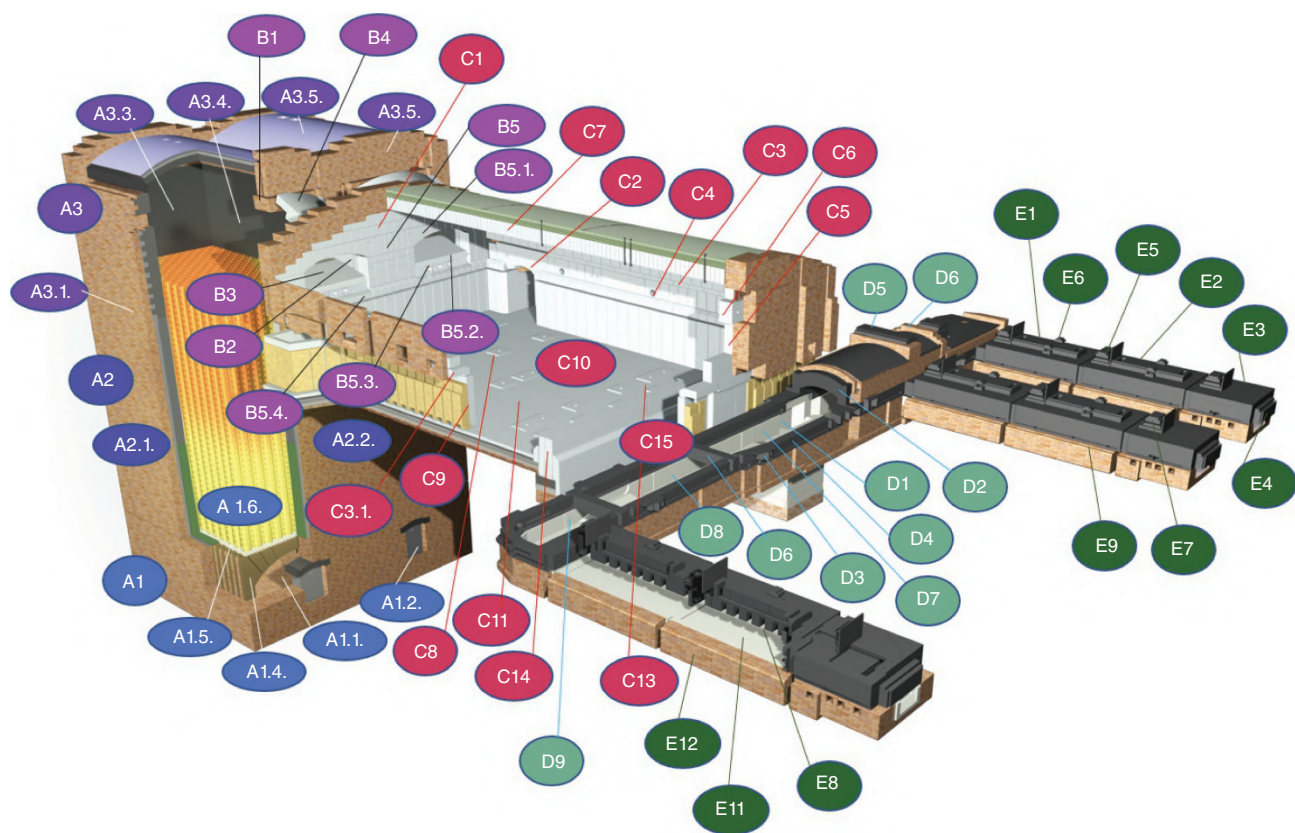


Figure 6 Individual components of an end-fired regenerative furnace.

A. Regenerator: 1. Downpart: 1.1. bottom, 1.2. wall with cleaning openings, 1.3. flue gas channel (not visible here), 1.4. rider arch, 1.5. spanner tiles and transition layer, 1.6. checker work; 2. Central section: 2.1. side walls, 2.2. front wall (opposite side: rear wall; orange interior: checker work); 3. Head: 3.1. side walls, 3.2. entrance wall, 3.3. target wall, 3.4. middle wall, 3.5. crown.

B. Port neck: 1. regenerator entrance arch, 2. side wall, 3. bottom, 4. cap or crown, 5. port mouth: 5.1. entrance arch blocks, 5.2. apron block, 5.3. burner blocks with distance blocks in-between, 5.4. tuckstone block;

C. Melter: 1. back wall above port mouth (port gable wall), 2. doghouse entrance arch, 3. breast wall with backup layers and insulation, 3.1. tuck stone, 4. peep hole, 5. front wall or throat gable wall, 6. TV camera block, 7. crown, 8. doghouse with cover, 9. basin with soldier blocks and insulation, 10. melting end, 11. tank bottom, 13. bottom electrodes, melting end, and barrier boosting, 14. weir or dam wall, 15. refining end, 16. throat, 17. riser with distributor entrance;

D. Distributor: 1. entrance zone, 2. center forced cooling devices, 3. peep hole, 4. pencil burner lining, 5. radiation opening, 6. zone dividing wall, 7. basin and bottom, 8. heating/cooling zone, 9. alcove as heating zone.

E. Feeder: different components not explained in detail.

perfectly closed. On the other hand, the port neck must ensure an optimum energy supply to the glass bath and also, in combination with burner arrangements, low NO_x values, while preventing critical corrosion of the breastwall and/or crown in the melting end. On the furnace side, these functions are exerted by the *port mouth*. Its bottom is generally lined with AZS and its other parts also of AZS material for glass containers or of other materials such as mullite or magnesia (actually made up of 80% MgO along with Mg aluminates, silicates, ferrites, etc.), which are outwardly insulated with differently graded materials.

On the regenerator side, the entrance bears the highest load because of the contrasting temperature conditions of the firing and flue gas phases and of chemical attack from fuel and batch vaporization. The regenerator head with its special volume ensures that the flue gas is well distributed into the checkers to store in 20–30 minutes a maximum of heat to be then transmitted to the combustion air. The same applies to cross-fired furnaces, with the difference that the flue gas leaves the superstructure on the opposite side and then preheats the opposite regenerator side. This arrangement does not apply to recuperative furnaces and oxyfuel furnaces with continuous and permanent firing from either side.

In the overall stability of the regenerator walls, expansion in both horizontal vertical directions is considered. The lower part of the regenerator, the *downport*, has openings for cleaning. Its *ridger arches* and then *spanner tiles* and transition layers are mainly made of fireclay bricks; sillimanite, high-quality sillimanite, or even mullite or silica then become employed when the flue-gas and combustion-air profiles reach a temperature of about 800 °C. The checker rests on this basis. Its elements have been designed in various ways to optimize gas flow. The most common are the chimney-block and cruciform checkers, whereas straight basket-weave and staggered grid packing are also alternatively used outside Europe. Not only are higher-quality refractories successively implemented but they also must be compatible with the fuel used and the batch composition, but their thickness increases up to the regenerator head whose target wall is disproportionately stressed in comparison with the port neck.

The reversing unit separates the combustion-air from the flue-gas flow. Combustion air is sucked up via a fan and blown in via the air-connecting box of the reversing unit to pass through the downpart regenerator, to be preheated in the checkers, and eventually to reach the regenerator head from where it enters the melting end through the port neck. As for the fuel, it is brought through the port neck bottom by a special lance, located laterally in the port mouth or beneath the port-apron block, to the burner blocks where the flames form and are shaped.

Since the entire system is hydraulically connected, it is of vital importance for end-fired and cross-fired furnaces that the reversing process be smooth and gentle not to cause level fluctuations at the melting end, which would propagate downstream. In end- and cross-fired furnaces, one can reduce the impact on the glass level by igniting burners and burner ports at staggered intervals. In end-fired furnaces, the U-shaped flame is deflected at the throat gable wall and then passes through the other port neck.

4.3 Recuperators

Ceramic systems are often operated with a *falling* flue-gas flow. When they are brand new, heat from the flue gas exchanged in cross flow via shaped ceramic bricks brings combustion air to 1000–1150 °C, a range that almost reaches that of regenerators. When the system ages, however, complete separation between the air and flue-gas flows is no longer achieved so that preheating temperatures decrease and more air must be supplied to ensure the stoichiometry of the combustion reaction. In addition, dust deposits from the batch in the upper layers corrode their ceramic bricks and minimize heat exchange. Brief interruptions of the combustion-air flow due to power failures also affect the tightness of the systems because of overheats in some parts of the recuperator and then of the formation of cracks and joints upon gentle restart after shutdown.

Metal recuperators thus tend to be preferred because of the intrinsic fragility of ceramic systems. They can be designed with rising as well as with falling flue-gas flow. The former design is frequently chosen when condensates and re-sublimates form since gravitation bring the solid particulates back into the hot section from where they can be removed, when almost liquid, via special openings in the recuperator bottom. This design is also often used when a lack of emission requirements allows the flue gas to be discharged freely. In this case, the control of the furnace-pressure dampening and the chimney installed behind the recuperator are used permanently, and not solely in case of emergency as with other systems. Falling flue-gas is in contrast frequent to integrate an existing channel that leads through a filter to the chimney. The disadvantage is that condensates and re-sublimates forming upon cooling of the flue gas can accumulate or deposit on recuperator parts, reducing heat exchange, lowering the preheating temperature, and eventually causing slow plugs up and furnace problems.

Metal recuperators are basically of two kinds, which can be combined in different ways to increase preheating temperatures from 650 to 750 or even 800 °C, the highest working temperatures of current alloys. Higher temperatures could in principle be reached with ceramic

compensators before the flue gas temperature has reached a range at which steel may then be used. The unsolved problem is that ceramic refractories should be thin-walled to be good heat exchangers, which is problematic for brittle materials and would result in short service lifetime.

With *double shell* or *gap* recuperators, heat exchange by radiation and convection takes place between two concentric stainless-steel shells insulated with ceramic fiber and rock wool, the flue gas and combustion flowing directly or counterflowing in the inner and outer shells, respectively. To increase exchange surface, and thus heat flow, baffles or checker plates are fitted to the inner tube. These recuperators can also be used for preheating natural gas or pure oxygen up to certain temperatures. For lead glasses, preheating temperatures are generally limited to 450 °C, otherwise the recuperator would be rapidly destroyed by Pb-bearing flue gases. The *tube-bundle* recuperator whereby combustion air flows in small tubes included in the big one of flue gas is by far more expensive but can be used in higher temperature ranges without any problem. The bundle of tubes is often inserted in a part lined with refractories. Also here the tubes are corrugated to increase the surface, so a larger heat-exchanging surface for the air to be preheated is created.

Safety systems are an important aspect for all recuperators because overheating often cause distortions and cracks, which result in leaks through which the flue gas and combustion air mix. In addition, the air fan must have a permanent power supply because any interruption of the flow of the combustion air must be avoided. Another safety device is a flap opening automatically in case of power failure, through which cold air is sucked into the system to protect the inner shell. This system can be combined with a separate cooling or injector fan to achieve better cooling. Depending on the design of the entire system and on working temperatures, the combustion air could become too hot. The inlet section can thus be cooled, and the air that is not required for combustion and has already been preheated is simply “blown off.”

4.4 Flue-Gas Channels

The waste gases are evacuated by channels at about 600–300 °C to the chimney after having given away most of their heat to a recuperator and/or a flue-gas purification system. To prevent concrete from overheating, cooling slots are frequently installed underneath the channel. Different grades of refractories are selected as a function of the predefined temperature of the flue gas, of possible corrosion, and also of the local economic conditions. For fast, solid, and tight construction, the side walls and the arches of the channels should be completely or at least partially cast especially for complicated and angular

designs. But prefabricated parts are much helpful to reduce the erection time whereas traditional brickwork is generally chosen along with adequate thermal insulation in countries where labor cost is low.

Not surprisingly, recuperative and oxyfuel furnaces require fewer devices to be installed in the channels compared with regenerative furnaces. Only the outgoing pipes for the heat exchanger and the waste heat-recovery systems or filters are taken into consideration, sometimes along with the furnace pressure-regulation device. This happens when this pressure is not adjusted via a kind of induced draft or by means of cold injector air that expands in the hot flue gas current and, thus, creates a kind of counterpressure.

If flue gas is very wet and the potential for condensation is high, temperatures up to the filters and chimneys must be carefully checked in view of potential condensates. Within given temperature ranges, special sections and areas are inserted in the channels to reduce the flue-gas velocity so as to facilitate dropping of the particles. In oxy-fuel furnaces, a widened flue-gas channel often serves as a quenching chamber to cool down the flue gas with water or cold air. A kind of “pre-cleaning” of the flue gas is then facilitated if this quenching takes place at the right speed and temperature.

In regenerators, flue-gas reversal stations must be carefully designed. Because they are close to the regenerators, they are made with gray cast-iron slides that must run smoothly on rails to keep sealing tight. If not, ingress of the so-called *false air* would be problematic as it would, for instance, adversely affect reduction of NO_x emissions. Because of temperature changes made every 20 minutes, the stresses induced enable very sturdy connections between the stations and channels to avoid any false-air ingress. In modern reversal stations, a simple mechanical safety device ensures that the flue gas is released on one side at the same time that the combustion air is introduced on the other. For big cross-fired furnaces, it may be preferable to have several smaller reversing stations instead of a big one for better handling and more targeted distribution of combustion air. This applies specially to float furnaces for which up to eight sectional regenerator chambers allow the energy input and the temperature distribution along the longitudinal furnace axis to be accurately controlled. Regenerators without internal separation walls are less expensive and easier to operate, but also less effective in the control of longitudinal energy input.

In end-fired furnaces, a new concept has prevailed since the 1990s. It was designed fortuitously – and then found more efficient – when some local configuration prevented the usual one from being implemented. It consists in letting the flue-gas channel pass beneath the melter to reach the port neck. The disadvantage of equipment

damaged in case of a glass leakage is minimized by an appropriate structure for the bottom of the melting end. As for the advantage, it is a more even and continuous flow that results in a reduced energy consumption and slower furnace aging. With units getting bigger and bigger, end-fired furnaces now benefit from a similar solution whereby three or four sub-channels are used depending on furnace size. A targeted “regulation” of the flow through the diverse parts of the regenerator is facilitated in this manner because the temperature profile in the regenerator can be controlled during the firing phase, thanks to the several ways in which the combustion air can be introduced. With such subcanals, however, ways should be carefully designed to clean the regenerator bottom from condensates and dusts.

5 Furnace Design

5.1 General Considerations

Depending on local situation, the first step consists in determining the furnace type and size and the energy to be used that would yield the best operating results as a function of the costs of energy and raw materials as they may be guessed over periods of time reaching now from 15 to 20 years. Although electrical boosting should in principle be kept as low as possible, it is more advantageous when electricity prices are lower near nuclear power stations or hydropower plants. By making the superstructure taller, one can increase the energy input in such a way that the specific load increases to a certain extent but the gain has to be balanced against higher construction and refractory costs and also higher heat losses. The issue is again considered whenever additional investments or repairs are to be made. In India, where labor and refractory costs are low compared with those of gas or oil, large regenerators are built to reduce energy consumption as much as possible. In Europe, the solution is sought more pragmatically to come close to the optimum in every respect.

Market conditions are in addition relevant for container glass. In the United States, very big Triple-Gob or Quad-Gob IS machines are often used to produce the same kind of container for more than half a year with a constant, low cullet fraction. Tanks seldom need a big wall; they are usually a little bit deeper and their specific loading capacity is a little higher but they require a well-designed working end with ample volume for good control of glass conditioning. In Europe, the available cullet fluctuates daily on the market so that its fraction incorporated varies accordingly. Melters must then be very flexible whereas Quad-gob IS machines are not common and used only for small items up to about 150 g. These melters

therefore require various tools. A wall is an important element whereas the refining end has to accommodate tonnage leaps during production. A big volume is essential to serve as a buffer storage: for a fully equipped 90 m² melter, an overall tonnage of 275 tpd might have leaps of about 50 tpd so that the working end must be designed as a kind of distributor channel to supply well-conditioned glass to 3–4 IS machines. For float or fiber glass, in contrast, melter design does not differ so much in Europe and America.

5.2 Empirical Guidelines

Most helpful to the furnace designer are general empirical rules that are part of the company's know-how as well as design criteria also based on experience. Not following them makes it difficult to manufacture a marketable product or to keep energy consumption, hence production costs, within reasonable limits. Although they depend on glass types, many are valid for all furnace types using fossil fuel as the main energy source. In furnace engineering parlance, an important parameter is the *load* (Chapter 9.8), which has already been mentioned and is the production rate per unit of surface area expressed in tons per day and square meter (t/d.m²). In furnace design and construction, a modified quantity, the so-called *fossil load* plays a key role. It is defined as the fraction of the *load* sustained by the input of fossil fuel energy alone. Reaching a sufficiently high fossil load is the initial objective of furnace design; it is determined by the melting area, the length to width ratio, the height of the crown, the burner configuration, and many other construction details. The load ultimately envisaged is chiefly achieved by boosting (typically 5–30% depending on the type of glass). For this purpose, the configuration of electrodes and the dimensions of the melting space have to be designed accordingly as will be illustrated in the next section.

The more difficult it is to melt a specific glass, the more additional installations and tools need to be integrated if a high glass quality is desired. Of utmost importance in this respect is a long enough residence time in the *melting end*, including the refining part of bank, and not in the whole melter as commonly assumed. Depending on cullet fraction, glass quality, and tonnage leaps, between 18 and 20 hours are assumed to be optimal for container glass, out of average total 24 hours spent in the melter. For tableware, these figures are 26–28 and 30 hours, and they should be higher than 48 hours for special glasses.

The higher the wall, however, the more attention must be paid to avoid a stagnant area, for example, with bubbling or by boosting, which in addition stabilizes the convection current, especially in big furnaces. Boosting is in addition a good tool for modifying the temperature of the

throat inlet, the riser, and further the entrance temperature of the distributor. The higher the planned job changes in terms of tonnage differences and the more frequently these are to be put into effect, the higher an installed dam wall has to be and the deeper the refining part has to be depending on glass type.

Regarding melter geometry, the higher the specific total load of the melting end (fossil and electric proportion), the deeper the melting end must be. The narrower and smaller ($<50 \text{ m}^2$) the melting surface, the lower the glass bath must be and the lower the specific melting output can be.

The darker the glass color, the lower the fossil melting load (flint/amber/green, some green colors can only be melted with a proportion of electric boosting or if a bubbling system is installed).

In all cases, the customer's practice is of vital importance. If side electrodes are integrated in the soldier blocks of the melting end, boosting can be used when needed with a certain basic load. But dirty bottom glass is stirred up if boosting is switched on again after a certain downtime, which first leads an increased number of seeds and inclusions. With a bottom boosting system, the bath depth must not be too low otherwise no efficient convection current can be sustained. On the other hand, maintaining the required temperatures in a deeper bath can require continuous boosting. But bottom boosting is not always compatible with a high cullet fraction because introduction of metal impurities may result in leakage and total loss of the furnace.

Although float-glass furnaces have enormous dimensions, their capacity can be compared with those of container glass. The melting part can be exposed to a specific load up to 2.5 t/d.m^2 depending on size, color, and cullet fraction. Bubblers are used for tinted glass, which are inserted to a depth of about 600 mm into the glass bath. An advantage of bubbling systems available on the market, as proposed by F.I.C. UK, is that they can be activated as a function of the color of the glass melted. Another current trend is to use more and more boosting systems with up to 2.5 MW capacity in single circuits and up to about 6 MW maximum capacity to make optimum use of the operating systems. The refining part of such a float glass furnace must also be obviously able to handle this additional capacity, the same applying to the waist and working end. Specific loads up to about 4.5 t/d.m^2 in the refining part and up to about 5 t/d.m^2 in the working end are now not uncommon.

5.3 Increasing the Specific Load: An Example with Amber Glass

The influence of the operating parameters on production costs for different overall loads per square meter of

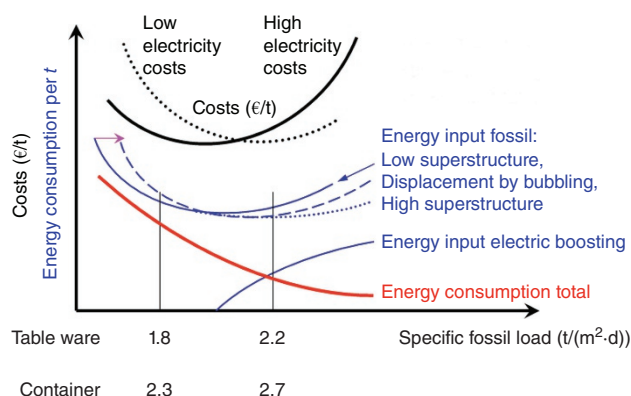


Figure 7 Energy consumption as a function of specific load (t/d.m^2) used to optimize economic furnace design for tableware and container glasses.

melting surface will be illustrated for tableware and container glass for which the energy optimum is for fossil loads ranging from 2.3 to 2.7 t/d.m^2 (Figure 7). When producing amber glass with 35% cullet, a small 45 m^2 end-fired furnace can be loaded with about 2.35 t/d.m^2 and heated with fossil fuel only to produce 105 tpd of good-quality glass having between 30 and 60 seeds/100 g, which complies with the European standard. Because it is fossil fired, the furnace cannot be very deep as bottom temperatures would be too low and glass quality insufficient. With a dam and bubblers, production could increase to 110 tpd with the same cullet fraction and glass quality, and to 135 tpd with additional boosting. For a similar furnace twice as great, i.e. of 90 m^2 size, the specific load can be 2.45 t/d.m^2 from the start, thus producing 235 tpd. This figure could be brought to 265 tpd with side boosting and to even 275 tpd in combination with bottom boosting, in which case the bath depth has to be increased.

Up to 475 t/d of the same amber glass can be melted in a 180 m^2 end-fired furnace whose length of about 18 m imposes from the start an additional tool to stabilize the convection current. Although about 500 tpd can be attained with bubbling, a designer will prefer bottom boosting. Depending on the number and diameters of the electrodes, up to 2600 kWh can be supplied directly into the glass to increase capacity to 570 tpd. The overall installed boosting capacity obviously needs to be higher. With additional boosting in the melting end, preferably at the bottom for a large size, the overall tonnage can be increased from 700 to about 720 tpd provided that the bath depth has been increased accordingly.

With a 90 m^2 oxyfuel furnace, one could certainly melt up to 250 tpd of amber glass depending on oxygen purity. With regard to energy, the efficiency would at first sight certainly be the best but the energy required to produce

oxygen would of course have to be included. Also note that the figures reported for amber glass would not apply to flint glasses, for which the specific load could be higher, and for green glass, which does not melt so well and for which the iron and chromium contents have to be taken into account. Regardless of glass color, the load broadly increases in the order lead crystal, crystal, cover, and aluminosilicate glass, followed by fiber, borosilicate, and float glass, the highest loads being achieved with container glass. In general, loads can be increased by boosting, often in combination with bubbling. In summary, these amber data are only rough guidelines, which can also vary much for a given type of glass with the raw materials used and their purity. Hence, many factors must be considered to estimate which particular configuration should be most profitable for a given type of production.

6 NO_x Emissions

An NO_x value of 800 mg/Nm³ for an 8% O₂ content and a dry waste gas represents 1.2 kg of NO_x per ton for container and float glasses. This figure was regarded as a magic limit way out of reach in the 1990s. At the price of an increased energy consumption, it is nowadays the limit in front of the chimney set in Germany whereas environmental authorities aim at 500 mg/Nm³ for new regenerative end-fired or cross-fired furnaces [5]. For oxyfuel furnaces, the limiting value is not referred to the Nm³ flue gas, but to the amount of glass melted.

These pollutants form from nitrogen in the fuel and the raw materials, especially when nitrates are present in the batch. The formation of NO_x from atmospheric oxygen and nitrogen can take place by different routes [13]. The first identified were the so-called Zel'dovich mechanisms [14], namely a slower reaction



followed by the much faster



But NO can also form through reactions with OH radicals or via *prompt* mechanisms [15] taking place in the flame front near the burner surface via attacks of carbon or hydrocarbon radicals on N₂ molecules such as



The NO_x emission levels thus greatly depend on the fuel used, (excess) oxygen content, and CO content in the flue gas. Because the furnace itself also matters, other factors to be considered are its length to width ratio, superstructure height, regenerator size, and number and type of burners as emissions are lowered with fewer burners, reduced superstructure temperatures, and lower preheating temperatures of the combustion air. If more than three burners per port are used for end-fired furnaces, an increase of the NO_x values from 100 to 300 mg/Nm³ NO_x per additional burner is to be expected, depending on the burner type and design. Similar correlations can be seen in cross-fired furnaces.

An efficient method to lower NO_x emission is to increase the CO content in the regenerator head (Table 4), but values higher than 1500 ppm may cause checker breakdown via disintegration of the refractories as a result of microcracking or even powdering. The cause is the formation of iron carbides between 400 and 600 °C from the carbon produced by the Boudouard reaction



This reaction takes place by chemisorption of CO and its subsequent decomposition catalyzed by active Fe atoms produced by the reduction of iron oxides present in the refractories, which then participate in a second reaction to produce iron carbides [16].

Alternatively, mixing the combustion air with part of the exhaust waste gas in the downpart of the regenerator can help to lower NO_x emissions right from the reaction

Table 4 Correlation between CO and NO_x contents.

Position	CO content (ppm)		
Regenerator head	<50	<300	600–800
Regenerator downpart	None	<50	100–300
Chimney front	None	None	<100
	Corresponding NO _x content (mg/Nm ³)		
Two burners installed	550–750	500–600	450–500
Three burners installed	700–900	600–800	<700

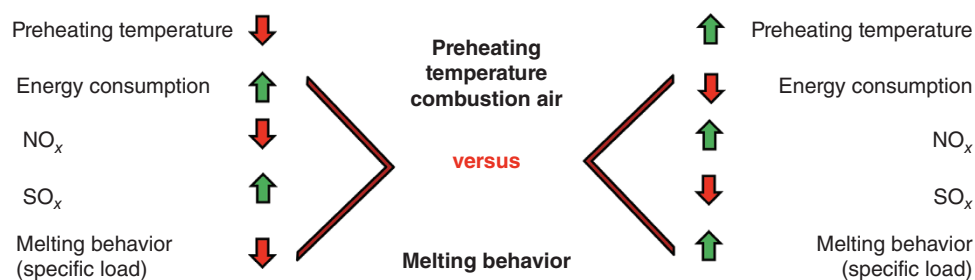
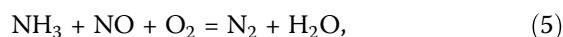


Figure 8 Interplay of factors involved in NO_x and SO_x emissions.

with the fuel at the port mouth. But the complex balance of factors to be considered also involves SO_x species (Figure 8). A lower air preheating temperature, for example, results in lower NO_x levels, but then both the energy consumption and the SO_x content in the flue gas increase and the achievable pull rate decreases, and vice-versa.

Experienced practitioners know so well these correlations that primary reduction of NO_x has almost reached its limits; potential improvements might concern only burners whose emissions could be brought down to about 300 mg/Nm^3 per unit. Further, NO_x decreases should thus rely on shifts of the gas-phase equilibria by selective non-catalytic reduction reactions [17]. A relevant reaction is [18]



which is beneficial from 1000 down to 700 and 870°C depending on whether or not H_2 is added to the system. Temperatures higher than 1000°C should be avoided, however, because the adverse reaction



then predominates. Considerable reductions of the NO_x values in front of the chimney can thus be achieved through injection of ammonia or ammonia solutions into the flue gas within the right temperature window, but the investment and operating costs can amount to about 100 k€ per year depending on plant size and flue gas volume flow to be treated.

7 Perspectives

From the mid-twentieth century, a general trend in glass-making has been to develop bigger units as exemplified not only for float but also for container glass for which the IS machines keep increasing in size and production volume (Chapter 1.5). Owing to increasing industrial concentration, this trend will likely continue in the future so that small furnaces will probably remain only for

producing special or highest-quality glasses. Multicolor furnaces for container glass are, for instance, designed to be highly flexible – and therefore smaller – with only one or at most two IS machines to speed up reactions in response to market situations. For usual container glass, the size of cross-fired furnaces will in contrast approach 230 m^2 to ensure an output of 1000 tpd. For float glass, 1000 tpd will no longer be a limit, thanks to future improvements brought to the tin bath and annealing lehr, and especially to faster operations at the cold end where the ribbon is cut and withdrawn. For lower outputs in the 600–700 tpd range, end-fired furnaces will be increasingly built in view of their enormous savings in investment costs. Once they have been implemented and the right conclusions drawn, these furnaces will certainly become larger.

Progress will also be made for the refractories. To summarize the considerable improvements already brought to their properties, it will suffice to state that in the 1930s their campaign lives and maximum temperatures were only 11–13 months and 1400°C [1]. By comparison, the service life of furnaces currently reaches about 15 and 20 years for container and float glass, respectively, during which there can be short periods of hot repair of local defects in the upper structure or, more rarely, complete shutdown and release of melt for cold repair of critically corroded areas in the lower structure. For fossil-fuel furnaces, more ceramic-bonded AZS materials will certainly be used and additional advantages will accrue if the basic idea of compound materials such as the sandwich or zebra blocks is picked up. For the superstructure, 190–250 mm blocks of pure AZS could, for example, be replaced by 75–100 mm AZS sandwich blocks, which would ensure, in combination with high-alumina refractories, the same stability and application limits. Considerable savings in investment costs could be made in this way, which would in addition limit tapping expensive zirconium resources.

In the past decade, alternative melting technologies have been thoroughly developed with the aim to increase both energy utilization and production efficiency. These

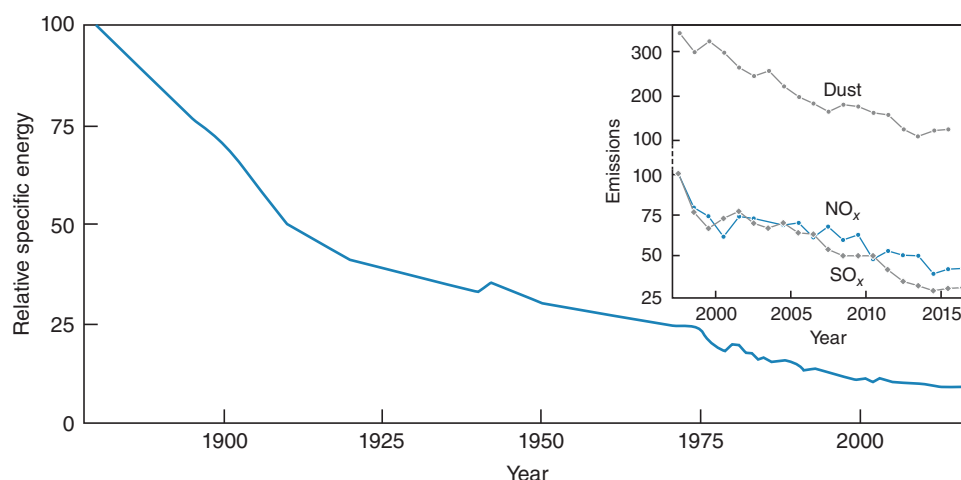


Figure 9 Evolutions of overall energy efficiency and emissions of NO_x , SO_x , and dust over the years. Source: Data from <http://www.agc-glass.eu/en/sustainability/environmental-achievements/air>

approaches comprise: (i) submerged combustion technology whereby burners deliver in a bubbler-like manner their flames from the bottom of the melting space directly into the melt; (ii) inflight technology whereby a finely ground batch is delivered directly into the flames; (iii) top vertical burners whose flames impinge on the melt surface. Even though the last one is now applied by several producers, for example, for fiber glass, none of them have fared significantly better than conventional technologies with respect to the intended goals.

From an environmental standpoint, one should finally stress the impressive nature of the improvements brought over the years (Figure 9 and insets). The evolution of the energy efficiency is especially striking with more than ten times increase since 1880, whose leveling off might suggest that the intrinsic limits of current processes are being approached. This reduction of the melting energy from 5600 kWh/t in the 1930s to 1000 kWh/t today for container glass has been largely attributable to the improvements in refractory materials. Of more recent concern are the NO_x and SO_x emissions, which a company such as AGC has been able to decrease by a factor of 4 in 20 years. A similar trend is observed for the emissions of dust, which is mainly made up of sulfates. These reductions are achieved with filters. Whenever possible the dust collected is recycled as sulfate batch components.

But enormous investments remain to be made by the glass industry at large to comply with the legal requirements worked out by the EU for NO_x emissions because many plants do not benefit yet from up-to-date technologies. New development are also being made, for example, for big all-electric melters for which, however, another challenge will be really permanent energy sources. And it will be seen whether new procedures such

as thin-melting processes or submerged-burner systems will be more successful on the market than others that have been developed in the past. As for the move toward a CO_2 -free production, it would involve a still more difficult challenge as carbonates should be eliminated from the batch, which would require major changes in the raw materials used ever since the beginnings of glassmaking.

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9.8

Physics and Modeling of Glass Furnaces

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1 Introduction

Glass furnaces, their construction and operation, play a key role in industrial glass manufacturing for the obvious reason that the melting stage is the starting point of all further operations. The primary objectives of melting are (i) glass quality, (ii) production efficiency through a high production rate relative to the furnace size, and (iii) environmental sustainability, i.e. minimization of both energy demand per unit mass of produced glass and release into the environment of CO₂, dust, SO_x, NO_x, HCl, HF, etc. These objectives are actually somewhat conflicting [1] as travel comfort, speed, and fuel consumption are in a car journey. Because the challenge consists in finding optimum compromises between the primary objectives, any furnace necessarily depends on the production intended and on its volume and can in addition display specific construction features (Chapter 9.7).

Glass can be heated with either fossil fuel or electricity and melted either in tank furnaces operated continuously or in pot or crucible furnaces working discontinuously. All-electrical as well as discontinuously operated pot and crucible furnaces are relevant to the production of crystal glass tableware, specialty, and art glass. For insulation fibers (Chapter 9.3), some manufacturers use metallurgical-like *cupola* furnaces whereby a packed bed of coal is in direct contact with the raw materials and the melt. In the flat- and container-glass industries, however, continuously operated fuel-fired furnaces with an additional electrical boosting are largely prevailing. These furnaces will thus be the focus of the present chapter.

Hence, the fundamental physical principles governing the work of glass furnaces as heat exchangers and chemical reactors will first be presented in terms of the key parameters characterizing these functions. Next, the relevant heat balances will be set up with special attention to the determination of the heat transferred to the melt, which will be made through the theory of heat exchangers supplemented by a simple model of radiative heat exchange. From an economic standpoint, two fundamental questions will then be discussed, namely the dependence of furnace operation on the production rate and the input–output characteristics of the furnace as a chemical reactor. As a complement to the theoretical methods presented in Chapter 1.7, some practical aspects of furnace modeling will finally be discussed with emphasis on locally and temporally resolved pictures of the intrinsic heat and mass transfer processes involved.

Notations

The following dimensionless quantities are used:

ζ	temperature efficiency
NTU	number of (heat) transfer units
z_{HL}	heat capacity-flow ration between hot and cold stream

Energies and derived quantities (powers, heat fluxes) are specified by the following indices:

ex	exploited heat; it comprises the latent heat content of the melt at exit temperature and the reaction heat of the (mostly endothermal) thermochemical reactions of the batch-to-melt conversion
fire	heat exchanged with the furnace body, i.e. the batch, the melt, and the refractories
flue	heat carried by the flue gas leaving the combustion space and entering the heat-recovery system

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H	referred to the hot stream or the combustion space
ht	heat transferred across the hearth surface
in	energy input by fuel and electric boosting
L	referred to the cold stream or the melting compartment
re	heat recovered by the heat-recovery system
sf	total heat set free in the combustion space
stack	heat carried by the flue gas leaving the heat-recovery system
X	referred to the heat recovery system
w	wall losses, distinguished as w_H , w_L and w_X

2 Furnace Parameters

2.1 Basic Configuration of a Tank (or Hearth) Furnace

The majority of furnaces consist of a shallow basin whose dimensions $V_L = \text{length } L \times \text{width } W \times \text{depth } D$ are typically $V_L = 10 \times 6 \times 1 \text{ m}^3$ for container and $30 \times 10 \times 1.4 \text{ m}^3$ for float glass. This *melting space* is in direct contact with the *combustion space* of volume V_H whose cover is arched (the crown) and side walls are vertical. The subscripts H and L designating here *high* and *low* refer to the combustion and melting spaces, respectively, and will also be used to denote the corresponding mass flows, i.e. the hot and cold streams. Heat transfer from V_H to V_L takes place across the hearth area $A = L \times W$ such that a typical 5–20% share of energy is delivered to V_L by electrical boosting via submerged electrodes.

As a heat exchanger, the furnace operates along three principal temperature levels: first, the environmental temperature T_0 of about 25°C ; second, the constant exit or pull temperature T_{ex} of typically $1320 \pm 20^\circ\text{C}$ at which the molten glass leaves the melting space; third, the so-called adiabatic flame temperature T_{ad} , which denotes the highest temperature that could be reached if the entire heat set free in the combustion process were stored in a thermally isolated flue gas. Although this temperature is not reached anywhere in the combustion space, its thermodynamic importance stems from the fact that it plays a key role in the thermal efficiency of a furnace. The adiabatic temperature depends on the amount of energy carried by the fuel and recovered from the hot flue gas. It can thus be readily calculated from the heat capacity of the flue gas, whose variations with temperature may be accounted for by equations of the type $c_{\text{flue}} = A + B T + C T^2 + \dots$. Typical T_{ad} values are 2440, 2500, and $2880 (\pm 25)^\circ\text{C}$ for air-gas, air-oil, and oxy-gas firing, respectively. In contrast to T_{ad} , T_{ex} , and T_0 , the flue-gas exit temperature T_{flue} does not constitute a boundary condition of the furnace operation; it is rather determined by the actual heat-exchange process.

2.2 Units and Reference States

Masses will be given in metric tons, times in hours, mass flows in t/h, temperatures in $^\circ\text{C}$, and densities (ρ) in t/m^3 . For a glass melt, the density may be taken as 2.4 t/m^3 whereas its values are 1.288, 0.716, 1.965, and $0.804 \cdot 10^{-3} \text{ t/m}^3$ for air, natural gas, CO_2 , and H_2O , respectively. Gas volumes are conventionally referred to *normal conditions* defined as 0°C and 1 atm, which thus differ from the 25°C and 1 bar generally used for thermodynamic standard states. Although the 1 m^3 volume of an ideal gas under the former conditions translates into 1.106 m^3 under the latter, energies depend little on which reference state is chosen.

For example, the enthalpy of the reaction



termed the net calorific value H_{NCV} , amounts to 802.6 and 802.4 kJ/mol for the normal and thermodynamic reference states, respectively. Because the difference is negligible, energies may be calculated relative to the thermodynamic standard state as usual. They will be consistently given in kWh for immediate conversions into electrical energy equivalents. Conversion factors with other units are $1 \text{ kWh} = 3.6 \text{ GJ} = 860.4 \text{ kcal} = 3412 \text{ BTU}$.

Heat capacities are given in $\text{kWh}/(\text{t}\cdot\text{K})$ unless stated otherwise. In heat transfer, what actually matters is the product of the mass flow (m') and heat capacity $m'_H \cdot c_H$ and $m'_L \cdot c_L$ of the hot and cold streams, respectively, which are thus expressed in kW/K .

3 The Physics of Glass Furnaces

3.1 Key Indicators

Referring to Chapter 1.1 for a general description of the chemical processes that take place in furnaces, we will first consider only their thermal aspects. The overall thermal performance of a system (Figure 1) is characterized by three dimensionless quantities as key indicators. The first is the *temperature efficiency* ζ , defined as a dimensionless parameter in terms of the three aforementioned temperatures:

$$\zeta = \frac{T_{\text{ex}} - T_0}{T_{\text{ad}} - T_0}. \quad (2)$$

This indicator has the advantage of summarizing the ultimate result of the heat exchange process, i.e. the ratio of the temperatures of cold stream at exit and hot stream at entry, both relative to the environmental temperature. It is a special feature of glass furnaces – in contrast to heat exchangers in general – that the value of ζ is fixed: For a given fuel and combustion mode (air-gas or oxy-fuel),

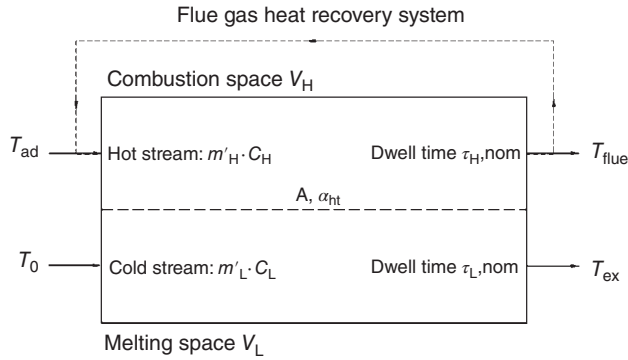


Figure 1 Fundamental parameters controlling a furnace in its dual functions as a heat exchanger and a chemical reactor over a hearth area A with a heat transfer coefficient α_{ht} ; adiabatic, exit, and flame temperatures, and heat capacity mass flows and dwell times of the hot and cold streams.

hence, for a given T_{ad} , the temperature efficiency ζ is fixed by the technological requirement to keep the glass exit temperature T_{ex} constant within narrow bounds. For air-gas and oxy-fuel combustion, ζ assumes a value of about 0.53 and 0.46, respectively.

The second key indicator is the dimensionless heat capacity-flow ratio given by

$$z_{HL} = \frac{m'_H \cdot c_H}{m'_L \cdot c_L}. \quad (3)$$

In general terms, this indicator compares the power delivered by the hot stream to the power uptake by the cold stream at an infinitely large exchange interface or at infinitely fast heat transfer rate. An inspection of z_{HL} has direct practical consequences: if a furnace suffers from a heat capacity-flow mismatch, reflected by a z_{HL} very different from unity, then furnace performance cannot be improved by measures enhancing the heat-transfer rate (like reduction of a foam layer, use of strongly radiating flames, etc.).

The third key indicator is the dimensionless number of transfer units, NTU, which is a measure of the finite heat transfer rate across the hearth surface:

$$NTU = \frac{\alpha_{ht} \cdot A}{m'_H \cdot c_H}, \quad (4)$$

where A is the hearth surface area and α_{ht} the mean heat transfer coefficient between the combustion and melting spaces, expressed in $\text{kW}/(\text{m}^2 \text{ K})$.

These three indicators are linked by the relation $\zeta = f(z_{HL}, NTU)$. Algebraic formulae are available for simple geometrical standard configurations only (see Eq. 14a, b). Since ζ is kept constant in furnace operation, z_{HL} and NTU cannot be optimized independently; they rather depend on each other.

The overall mass flow performance of a system (Figure 1) is described in relation to the nominal (or geometrical) dwell time $\tau_{L,nom}$ of the cold stream in the melting space. It is simply defined as $\tau_{L,nom} = \rho_{melt} \cdot V_L / p$, where $p = m'_L$ is the glass production rate. It is of the order of 20–40 hours. The dwell time $\tau_{L,nom}$ allows one to describe the response of a furnace as a chemical reactor in terms of a dimensionless timescale $z = t/\tau_{L,nom}$, hence, to compare furnaces of different sizes and production yields. The nominal dwell time of the hot stream $\tau_{H,nom}$ is smaller than $\tau_{L,nom}$ by approx. four orders of magnitude. It suffices here to state that it is about 5 seconds.

3.2 From Heat Balance to Furnace Efficiency

Modern furnaces include flue-gas heat-recovery systems (Figure 2). Their heat balance may be described in three different ways: (i) as a power balance, P in kW; (ii) as a balance of energies per ton of produced glass, H in kWh/t; (iii) or as heat fluxes, q , in kW/m^2 per unit hearth area A . These quantities are mutually related by $P = H p$, $q = H r$, $r = p/A$, where p and r thus denote the production rate expressed in t/h and in $\text{t}/(\text{m}^2 \cdot \text{h})$, respectively. Illustrating that the compromises made between quality and throughput depend on the type of glass produced, furnaces typically have r values of 0.13–0.16 $\text{t}/(\text{m}^2 \cdot \text{h})$ for containers but only 0.07–0.10 $\text{t}/(\text{m}^2 \cdot \text{h})$ for float, corresponding to 3.2–3.8 and 1.7 to 2.4 $\text{t}/(\text{m}^2 \cdot \text{d})$, respectively.

Operationally, an important parameter is of course the power input $P_{in} = H_{NCV} \cdot V'_F$, where H_{NCV} is the net calorific value of the fuel and V'_F the volume flow of fuel under normal conditions. The net calorific value depends on whether or not the water of the flue gas remains

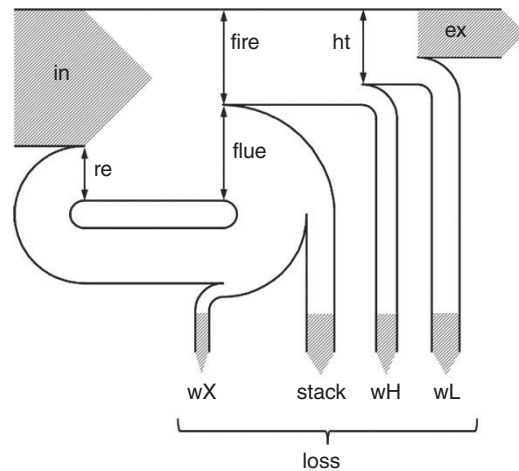


Figure 2 Heat balance of a fuel-fired furnace equipped with a flue-gas heat-recovery system; the exploited heat comprises both the latent heat content of the melt at pull temperature and the heat demand of chemical reactions of the batch-to-melt conversion.

gaseous. If not, the condensation heat must be taken into account into the gross calorific value H_{GCV} , which is thus about 10% higher than H_{NCV} (e.g. 11 vs. 10 kWh/m³) for natural gas. The difference has definite economic implications because the prices quoted by fuel suppliers refer to H_{GCV} whereas the amount of energy useful for the process is H_{NCV} .

With electric boosting, then $P_{in,total} = P_{in,F} + P_{boost}$ where the subscript F denotes fuel. For simplicity, this boosting will not be taken into account in the following although it would be readily accounted for. The useful power drawn from the furnace, P_{ex} , is also termed the exploited power. To account for chemical reactions within the batch and the heat content of the melt, one expresses it as $P_{ex} = H_{ex}p$. The parameter p is the production rate and H_{ex} is given by

$$H_{ex} = (1 - y_C) \cdot \Delta H_{chem}^\circ + \Delta H(T_{ex}), \quad (5)$$

where y_C is the amount of cullet per ton of produced glass, ΔH_{chem}° the standard chemical heat demand of the batch-to-melt conversion (referred to 25 °C, 1 bar), and $\Delta H(T_{ex})$ the heat content of the melt at the exit temperature T_{ex} .

The principal balance (Figure 2) then reads

$$P_{in} = P_{ex} + P_{loss}, \quad (6)$$

where the cumulative loss P_{loss} comprises all wall losses and the power carried by the flue gas when leaving the cold end of the heat-recovery system.

Both P_{in} and P_{ex} , and hence, by difference, P_{loss} , are thermodynamic functions of state. Because they do not depend on the actual paths of the combustion and melting processes, they can always be calculated accurately. The same applies to the overall efficiency of heat exploitation η_{ex}

$$\eta_{ex} = P_{ex}/P_{in}. \quad (7)$$

Two further balance equations are derived. The power P_{sf} set free in the combustion space amounts to

$$P_{sf} = P_{in} + P_{re} = P_{flue} + P_{fire}, \quad (8)$$

where the subscripts re, flue, and fire mean recovered from the flue gas, lost with it, and exchanged with the furnace body, respectively (Figure 2). For a given production rate p , P_{sf} is the power required to sustain the glass quality desired. If, for example, a problem occurs with the heat recovery system such that P_{re} goes down, then P_{in} has to be adjusted accordingly to sustain a constant P_{sf} .

Since P_{flue} is the power leaving the combustion space, it is the portion of P_{sf} that is not exchanged with the furnace body. The power actually exchanged with this body thus is

$$P_{fire} = P_{wH} + P_{ht} = P_{wH} + P_{wL} + P_{ex}, \quad (9)$$

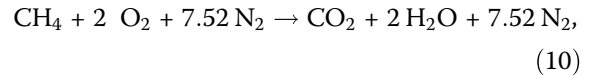
where P_{ht} is the power transferred to the melting space and P_{wH} and P_{wL} that lost to the walls.

Both Eqs. (8) and (9) are useful to pinpoint areas of strong and weak performances of a furnace, for example, in terms of the

combustion space efficiency	$\eta_{sf} = P_{fire}/P_{sf}$
heat transfer efficiency	$\eta_{ht} = P_{ht}/P_{in}$
efficiency of heat recovery	$\eta_{re} = P_{re}/P_{flue}$
furnace insulation efficiency	$\eta_w = 1 - (P_{wH} + P_{wL})/P_{in}$

3.3 Toward Energy Savings

As instructive as these quantities may be, their practical usefulness is limited by the uncertainties that beset their individual terms and thus make their evaluation more difficult than that of the power input P_{in} in Eq. (6). Owing to the complex structure of a real furnace (Chapter 9.7), calculations of heat transfer across the refractory walls yield rough estimates at best. Because P_{flue} and P_{re} are related to the volume flows of flue gas and combustion air, respectively, the cumulative wall losses $P_{wH} + P_{wL}$ can be better assessed from the difference between Eqs. (8) and (9). The temperatures T_{flue} (exit temperature of flue gas) and T_{re} (entry temperature of preheated air) need also to be known although their measurements are fraught with technical difficulties. In a first step, the volume flows V'_{flue} and V'_{air} must also be determined. For a hypothetically stoichiometric combustion, they are directly related to the flow of fuel V'_F and to the volume ratios n_{flue} and n_{air} of flue gas to fuel and air to fuel, respectively. In real combustion processes, an air excess λ of $\lambda = 1.02$ – 1.08 has to be used. When the simple combustion reaction is written



the coefficient $7.52 = 2(79/21)$ thus reflects the approximate composition of air with 79% N₂ and 21% O₂. It follows that $n_{flue} = 10.52$, $n_{air} = 9.52$, and $n_{air}/n_{flue} = 0.9$.

All these parameters are mutually related by the following equations, which also take into account the flow V'_{bg} of gases released from the batch:

$$V'_{flue} = (n_{flue} + (\lambda - 1) \cdot n_{air}) \cdot V'_F + V'_{bg}, \quad (11a)$$

$$V'_{bg} = (m'_{batch} - p) \cdot (V^{id}/M_{bg}), \quad (11b)$$

$$V'_{air} = \lambda \cdot n_{air} \cdot V'_F, \quad (11c)$$

$$P_{flue} = V'_{flue} \cdot c_{flue} \cdot (T_{flue} - T_0), \quad (11d)$$

$$P_{re} = V'_{air} \cdot c_{air} \cdot (T_{air} - T_0). \quad (11e)$$

Here, m'_{batch} is the mass flow of batch in t/h, $V_{\text{id}} = 22.4 \text{ m}^3/\text{kmol}$ is the volume of ideal gases, and M_{bg} the average molar mass of batch gases in t/kmol. From Eqs. (11d) and (11e), one determines the efficiency of the heat recovery system as

$$\eta_{\text{re}} = \frac{P_{\text{re}}}{P_{\text{flue}}} < \frac{n_{\text{air}}}{n_{\text{flue}}} \cdot \frac{c_{\text{air}}}{c_{\text{flue}}}. \quad (12)$$

The efficiency is always smaller than the product of the ratios $n_{\text{air}}/n_{\text{flue}}$ and $c_{\text{air}}/c_{\text{flue}} \approx 0.9$, which thus sets an upper bound of 0.81. If the wall losses P_{wX} are taken into account, lower values in the range 0.55–0.65 are actually obtained upon finite-time operation. Combining Eq. (8) and (11a–e) and solving for V'_{F} , one finally expresses the fuel demand as

$$V'_{\text{F}} = \frac{(1 - \eta_{\text{re}}) \cdot c_{\text{flue}} \cdot V'_{\text{bg}} + P_{\text{wH}} + P_{\text{wL}} + H_{\text{ex}} \cdot p}{H_{\text{NCV}} - (1 - \eta_{\text{re}}) \cdot (n_{\text{flue}} \cdot c_{\text{flue}} + (\lambda - 1) \cdot n_{\text{air}} \cdot c_{\text{air}}) \cdot (T_{\text{flue}} - T_0)}. \quad (13)$$

Through its different terms, this equation summarizes the various ways of saving energy by conventional means. Clearly, V'_{F} is minimized, if

- η_{re} is maximum;
- V'_{bg} is low, i.e. if one uses only raw materials releasing small gas volumes;
- furnace walls are well insulated, although the corrosion of their refractory materials is another factor to be considered;
- H_{ex} is minimized, for instance, with high amounts of cullet or raw materials having a low chemical heat demand in the batch-to-melt conversion;

- T_{flue} is kept low by adequate design for both burner and combustion technology;
- the air excess λ is also kept low, and an influx of *false air* (i.e. air sucked into the furnace by the action of the off-gas system) is avoided.

3.4 Intrinsic Heat Transfer

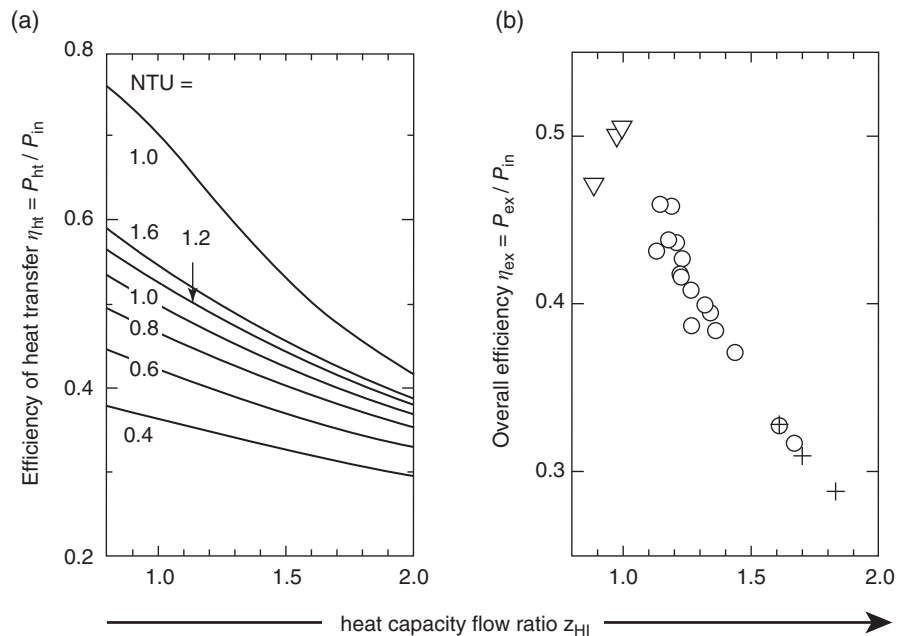
In the heat balance (Figure 2; Eq. (9)), a crucial term is the power transferred from the combustion to the melting space, P_{ht} . Because the conventional heat balance does not yield it directly, two different approaches can be followed. The first makes use of the standard equations for heat exchangers in terms of two of the aforementioned key indicators, namely z_{HL} and NTU:

$$\frac{P_{\text{ht,counter}}}{P_{\text{in}}} = \frac{1}{z_{\text{HL}}} \cdot \left[1 - \frac{1 - z_{\text{HL}}}{1 - z_{\text{HL}} \cdot \exp(-\text{NTU} \cdot (1 - z_{\text{HL}}))} \right], \quad (14a)$$

$$\frac{P_{\text{ht,co}}}{P_{\text{in}}} = \frac{1}{1 + z_{\text{HL}}} \cdot [1 - \exp(-\text{NTU} \cdot (1 - z_{\text{HL}}))]. \quad (14b)$$

Here, the subscripts *counter* and *co* denote the counter-directed hot stream and the codirected flow of the cold stream, respectively (Figure 1). Although the actual situation is more complicated, the overall performance is well represented by the arithmetic mean of these base cases (Figure 3a). The ratio $P_{\text{ht}}/P_{\text{in}}$ is a sensitive function of both the heat capacity ratio z_{HL} and the conditions of heat transfer as reflected by the NTU. From daily factory records collected over a period of two years, a survey of 23 different container-glass furnaces has revealed that

Figure 3 Efficiency of a glass furnace as a function of the heat capacity-flow ratio z_{HL} . (a) Power transferred to the melting space from the power input, $\eta_{\text{ht}} = P_{\text{ht}}/P_{\text{in}}$, for the indicated values of the number of transfer units (NTU); (b) overall efficiency $\eta_{\text{ex}} = P_{\text{ex}}/P_{\text{in}}$ of 23 container-glass furnaces at their optimum working point; circles: air-fuel end-port furnaces; crosses: air-fuel cross-fired furnaces; triangles: oxy-fuel furnaces.



NTU varies within a narrow margin from 0.5 to 1.2. Any technical attempt to enhance NTU can work only if the heat capacity flows are well balanced, i.e. if z_{HL} assumes a value close to 1 (Figure 3a). This is why the overall efficiency of heat exploitation calculated with Eq. (7) strongly decreased with increasing z_{HL} in this survey (Figure 3b).

Many furnaces suffer from unbalanced flow because z_{HL} is not well constrained. This applies especially to cross-fired air-fuel container-glass furnaces. On the other hand, the obvious advantage of oxy-fuel furnaces primarily rests much more on their excellent flow balance than on their elevated T_{ad} . Economically, however, this advantage has to be put into relation with the oxygen cost. It is true that one can improve the flow balance by operating a furnace at a small air excess, by avoiding false air, and by an adequate boosting. But z_{HL} is a basic parameter in furnace construction and combustion technology that is determined by the volume of the effective combustion space relative to the hearth area and by the effective cross section available for the flow.

For evaluating P_{ht} , an alternative approach rests on a simple radiation model (Figure 4). In general terms, the incident radiation (I) is transmitted (Tr), absorbed (Ab), or reflected (Rf): $I = Tr + Ab + Rf$. For heat radiation in a furnace, $Tr = 0$. According to Kirchhoff's law, the absorbed part is equal to the heat E emitted as thermal radiation so that $I = E + Rf$. As given by Stefan-Boltzmann's law, $E = \epsilon \sigma \cdot T^4$, where $0 < \epsilon < 1$ is the emissivity of the radiating volume or surface and $\sigma = 56.7 \cdot 10^{-12} \text{ kW}/(\text{m}^2 \cdot \text{K}^4)$ a universal constant. A black body ($\epsilon = 1$) at $T = 1000 \text{ K}$ thus emits $56.7 \text{ kW}/\text{m}^2$. The balance of heat radiation in a furnace can be described in terms of heat fluxes q normalized to the hearth area,

$q = P/A$ in kW/m^2 (Figure 4). The glass melt is approximated as a surface radiator, which is a good approximation for amber and Cr-green glass but a fair estimate at best for flint (white) glass. The heat-flux balance constitutes the following system for the four fluxes exchanged between the melt, gas, and crown (Figure 4):

$$q_1 = \sigma \cdot \epsilon_{\text{melt}} \cdot T_{\text{melt}}^4 + (1 - \epsilon_{\text{melt}}) \cdot q_2, \quad (15a)$$

$$q_2 = \sigma \cdot \epsilon_{\text{gas}} \cdot T_{\text{gas}}^4 + (1 - \epsilon_{\text{gas}}) \cdot q_3, \quad (15b)$$

$$q_3 = \sigma \cdot \epsilon_{\text{crown}} \cdot T_{\text{crown}}^4 + (1 - \epsilon_{\text{crown}}) \cdot q_4, \quad (15c)$$

$$q_4 = \sigma \cdot \epsilon_{\text{gas}} \cdot T_{\text{gas}}^4 + (1 - \epsilon_{\text{gas}}) \cdot q_1. \quad (15d)$$

The emissivities ϵ of the melt, gas, and crown are labeled accordingly. The heat flux $q_{ht} = q_2 - q_1$ is derived directly from the solution of this system (see Appendix). As an example, one can select $T_{\text{melt}} \approx 1500^\circ\text{C}$, $T_{\text{gas}} \approx T_{\text{crown}} \approx 1600^\circ\text{C}$; $\epsilon_{\text{crown}} \approx 0.5$, $\epsilon_{\text{melt}} \approx 0.6$, $\epsilon_{\text{gas}} \approx 0.13$ and 0.4 for air-gas and oxy-gas combustion, respectively [2]. Then the resulting fluxes q_{ht} are 60 and $73 \text{ kW}/\text{m}^2$, respectively.

3.5 Process Irreversibility and Rate Dependence

As useful as a heat balance may be, it is an incomplete representation of furnace performance. Its first shortcoming is it rests on the first Law of thermodynamics only so that a given amount of heat Q does not tell anything about its usefulness in a process. If 1200 kWh are, for instance, needed to melt one ton of glass, this heat must be available at the temperature T_{proc} of the process. If it were available at 500°C only, then bringing it to T_{proc} would reduce its amount by at least a factor $Q(1 - T_0/T_{\text{proc}})$. Because the entropy $S = Q_{\text{rev}}/T$ is a measure of energy degradation, only the fraction $P_{\text{in}}(1 - T_0/T_{\text{proc}})$ of the input power is then actually available. By contrast, electrical power $P_{\text{in,boost}}$ is available to almost 100%, thanks to extremely high Fermi or electron temperatures T_e in electrode materials, whose range $5 \cdot 10^4 - 10^5 \text{ K}$ implies that the term T_0/T_e is close to zero. As a second shortcoming, a heat balance presents a snapshot of furnace performance for only a given production rate. Time is not involved as an explicit parameter although it badly needs to be considered with respect to entropy production in any process involving transport phenomena and finite conductivities [3].

In other words, energy degradation and finite time constraint constitute a fundamental bottleneck for furnace operations. Obviously, large temperature differences ensure high heat-transfer rates and sustain high production rates. On the other hand, an irreversible transfer of heat Q from temperature T_2 to T_1 causes the creation of an entropy $\Delta S_{\text{irr}} = Q(1/T_2 - 1/T_1)$. Minimizing energy degradation thus calls for small temperature differences,

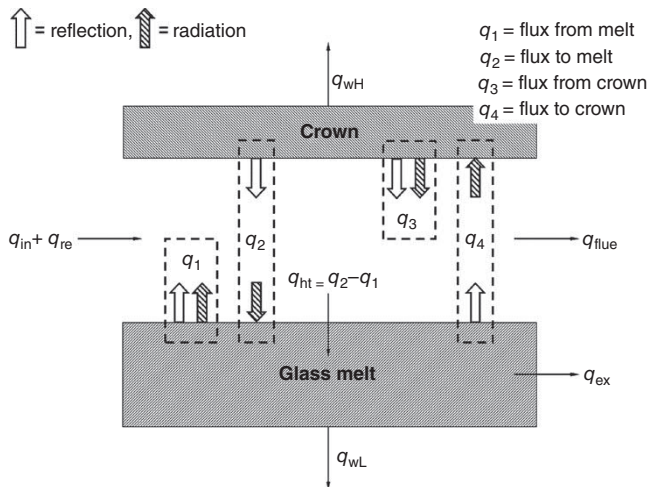


Figure 4 Model of radiative heat exchange between combustion and melting space; q = heat flux per unit hearth area; for meaning of subscripts, see also Figure 2.

for which energy efficiency would be maximum but production rates minimum. In glass parlance, overpull and wastefully low pull represent conditions of maximum temperature differences and minimum entropy generation, respectively. Trade-offs have thus to be found for operating heat exchangers in general [4] as well as glass furnaces in particular [5] (Figure 5).

When looking for such an optimum situation, one takes advantage of the simplifying feature that P_{in} is a linear function of the production rate until overpull is reached and glass quality degrades. This simple relation is obeyed in a surprisingly accurate way as illustrated by data for an end-port, air gas-fired furnace producing Cr-green glass for which the standard deviation of the measurements from a linear fit is only 270 kW (Figure 5b). With a batch containing 40% cullet and a hearth surface of 152 m², the exploited heat H_{ex} amounts to 487 kWh/t and the optimal working point empirically found is $p = 15.7$ t/h. The intercept of the linear fit represents the power input for a zero production rate whereas its slope is the amount of power per unit of production rate. Both parameters are characteristic constants of a furnace. The exploited power P_{ex} and the cumulative losses P_{loss} , see Eq. (6), are also shown in Figure 5b. The values of P_{in} and H_{in} at working point are marked with open circles. The value of P_{ht} (cross) at working point is derived from the flux q_{ht} calculated in Section 3.4. As for the energy demand per 1 ton of produced glass, H_{in} , it amounts to 1164 ± 17 kWh/t at the working point (Figure 5c).

In summary, every furnace possesses a working point representing an optimal compromise for a desired glass quality between production efficiency and energy utilization. Melting in a glass furnace is determined by three characteristic parameters: one is characteristic of the glass batch (H_{ex}) whereas the two others are specific to

the furnace, namely the intercept and slope of the P_{in} line (Figure 5b). This approach allows one to judge the quantitative effects of changes in both batch and pull rate and to compare the performances of different furnaces.

3.6 Reactor Working

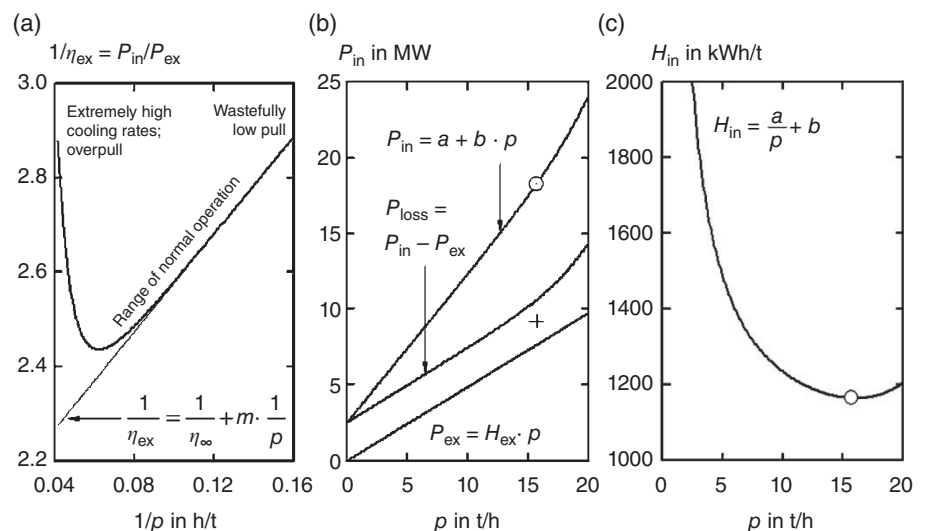
The melting space of a glass furnace is a chemical reactor where batch melting and sand dissolution take place, a defined redox state (and, thus, color) is established, and fining and refining are achieved (Chapter 1.3). An important question is thus to know the input–output characteristics of a furnace, i.e. how any change in the batch input affects the exiting melt. In a first pedagogical approach, it is useful to consider an actual glass furnace as intermediate between two reference kinds of chemical reactors, namely the *ideal mixer* whereby the feed is distributed instantaneously over the entire volume, and the *plug flow* which, in contrast, works on a strict first-in, first-out basis (Figure 6). For a real furnace, however, this approach is by far too simple.

In chemical engineering, the ratio between the amounts of a substance introduced by convection and diffusion in a reactor is characterized by the Bodenstein dimensionless number. In glass furnaces, this number $Bo = v L/D$ is about $4 \cdot 10^9$ for an average pull velocity $v \approx 0.4$ cm/s, a path length $L \approx 10$ m, and a diffusion coefficient of $D \approx 1 \cdot 10^{-7}$ cm²/s. For such a large value of Bo , internal diffusion processes do play an important role for local equilibration of concentration differences in a glass furnace, but they may be neglected with respect to the overall response.

Turning to the input–output relationship, we first note that a step input is converted to an exponential output in the ideal mixer whereas it appears as a step output in the

Figure 5 The influence of the pull rate, p , on the operation of a glass furnace.

(a) The different ranges of a heat exchanger clearly distinguished in a so-called chiller plot: η_{ex} , overall coefficient of performance, p , mass flow of the cooling medium, and straight line of the range of normal operation with an intercept $1/\eta_{\infty}$ and slope m . (b) Linear variation of the input power P_{in} as a function of the pull rate p , with an intercept $a = 2523$ kW and a slope $b = 1003$ kWh/t; H_{ex} = exploited heat; open circle: working point $p = 15.7$ h/t; cross: transferred power P_{ht} according to Section 3.4. (c) Typical hyperbolic variation of the overall specific heat demand H_{in} as a function of the pull rate.



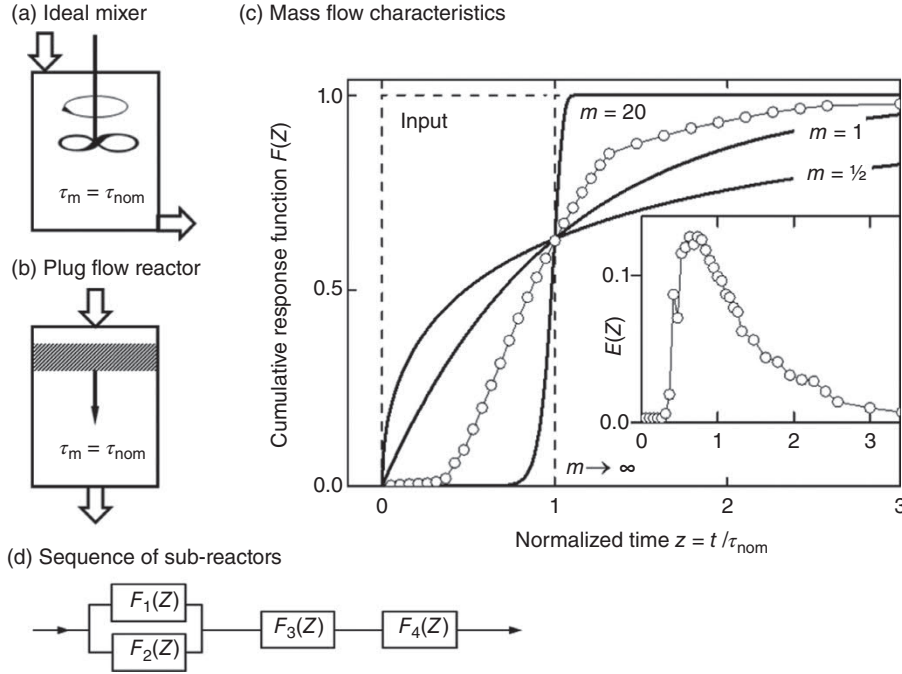


Figure 6 Mass input-output characteristics of chemical reactors. (a) Ideal mixer ($m = 1$); (b) plug flow ($m \rightarrow \infty$), the shaded area indicating concentration dissipation by a diffusion process; (c) influence of the parameter m of Eq. (18) on the cumulative response function $F(z)$; $m = 1/2$: dead water flow; symbols: tracer experiment for a container-glass furnace with a melting space volume of $V_L = 131 \text{ m}^3$ operated at a pull rate of 11.7 t/h , hence, $\tau_{\text{nom}} = 28.1 \text{ h}$; inset: differential response function $E(z)$. (d) Sequence of sub-reactors used to model $F(z)$ for the tracer experiments to within ± 0.008 (see Table 1); as $F_1(z)$ accounts for less than 1% of the response, it may be neglected in the numerical evaluation without loss of accuracy.

plug flow. Let then $z = t/\tau_{\text{nom}}$ be a dimensionless time-scale normalized with respect to the nominal dwell time τ_{nom} of the furnace (termed $\tau_{L,\text{nom}}$ in Section 3.1), and $c(z)$ be a normalized dimensionless concentration, $0 \leq c(z) \leq 1$. A step input is thus given by $c(z) = \theta(z)$, with $\theta(z) = 0$ for $z < 0$ and $\theta(z) = 1$ for $z \geq 0$. The output at time z is characterized by the differential and cumulative response functions $E(z)$ and $F(z)$, respectively:

$$E(z) = c(z) / \int_0^\infty c(z) \cdot dz, \quad (16a)$$

$$F(z) = \int_0^z E(z) \cdot dz. \quad (16b)$$

The mean dwell time τ_{mean} is then given by

$$\tau_{\text{mean}} = \tau_{\text{nom}} \cdot \int_0^\infty z \cdot c(z) \cdot dz. \quad (17)$$

For the response function, the use of an extended exponential function (KWW function) is recommended instead of the simple base cases “plug flow” and “perfect mixer.” Thus, the responses of both kinds of reactors may be presented by the common formulae:

$$E(z) = m \cdot z^{m-1} \cdot \exp(-z^m), \quad (18a)$$

$$F(z) = 1 - \exp(-z^m) \quad (18b)$$

and represented in the same way (Figure 6c). For the ideal-mixer and plug-flow reactors, the exponent m is unity and tends to infinity, respectively. An intermediate reactor thus is characterized by $m > 1$ whereas $m < 1$ refers to the so-called *dead water flow* whereby the reactor space is incompletely used because of short-circuit flow through the active volume. This situation yields a fast initial response and a protracted approach to complete replenishment of the volume at $F(z) = 1$, which is a much undesired production feature.

A quantitative assessment of furnace response is a key to an effective management of glass quality during job changes. Such responses can be studied through tracer experiments (Figure 6c) in which a small amount of CaCO_3 in the batch is, for example, replaced by SrCO_3 at $t = 0$ in a step-wise manner and samples of the melt are analyzed for Sr at the exit. For a real container glass furnace, in a first approximation, the output conforms to Eq. (18b) with $m \approx 2.5$. But it is obvious that the protracted approach to $F(z) = 1$ is not well represented in this way. The actual response is modeled by a combination of a finite number of sub-reactors. For this purpose, the response $F(z)$ obtained experimentally is plotted as $W = \ln[-\ln(1 - F)]$ vs. z (Figure 7). In this plot, as a common feature observed with many tracer experiments, the experimental furnace response data display a sequence of three to four linear subregions, suggesting a comparatively simple superposition of few sub-reactors

$$W_i = \ln(-\ln(1 - F)) = m_i \cdot \ln(z) + b_i, \quad (19)$$

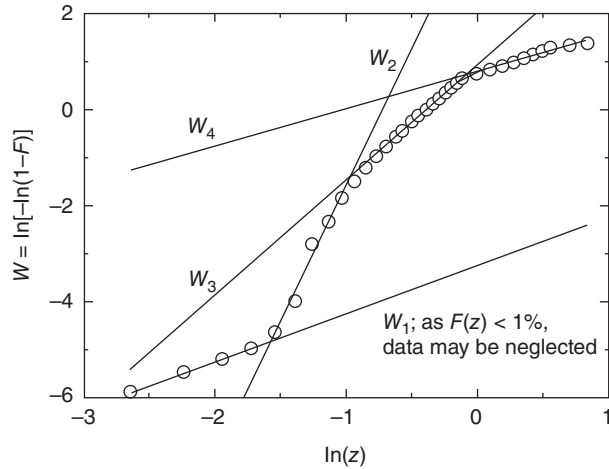


Figure 7 Experimental data of $F(z)$ (symbols) presented in a plot $W = \ln[-\ln(1-F)]$ vs. $z = t/\tau_{\text{nom}}$ and straight lines W_i , $i = 1, \dots, 4$ fitted to linear ranges representative of sub-reactors F_i .

$i = 1, 2, 3 \dots$ only (see Figure 7). The slopes of the individual straight lines yield the respective exponents m_i , the intercepts b_i yield the respective dwell times $\tau_i = \tau_{\text{nom}} \cdot \exp(-b_i/m_i)$, and the sub-reactor volumes $V_i = (\tau_i/\Sigma\tau_i) \cdot V_L$. If the slopes increase from $i = n$ to $i = n+1$, then W_n and W_{n+1} correspond to parallel sub-reactors; otherwise, they correspond to sub-reactors in series. The individual functions W_i are superimposed step by step to yield the cumulative function W_{cum} . Ultimately, the modeled response function $F_{\text{cum}}(z)$ is obtained as

$$F_{\text{cum}}(z) = 1 - \exp(-\exp(W_{\text{cum}})). \quad (20)$$

In the example treated here, the data with $F(z) < 1\%$ (sub-reactor 1) may be neglected in the numerical evaluation without loss of accuracy. As a result, the experimental data are represented at an accuracy of ± 0.008 by a superposition of the three sub-reactors 2, 3, 4 in series only. The final result obtained for the case discussed is shown in Figure 6d; the numerical parameters are listed in Table 1.

After the onset of the job change at $t = 0$, the output remains unchanged and the glass quality of the old job is maintained until a critical time $t_{\text{crit}} \approx 6$ hours is reached. A glass of an undefined intermediate quality is then produced until $z = 2.6$, i.e. 73 hours, after which the quality of the new job is again ensured.

4 Modeling of Glass Furnaces

4.1 General Remarks

Thanks to ever-increasing computer power, computational fluid dynamics (CFD) modeling of glass melting

Table 1 Characteristic dwell times τ_i , exponents m_i , and effective volumes V_i of sub-reactors $i = 2, 3, 4$, see Eq. (19), used to model the response function $F(z)$ of a tracer experiment performed on a container-glass furnace with melting space volume of $V_L = 131 \text{ m}^3$ operated at a pull rate of 11.7 t/h, hence, $\tau_{\text{nom}} = 28.1 \text{ h}$; $V_i = (\tau_i/\Sigma\tau_i) \cdot V_L$; F_1 and F_2 in parallel and in series with F_3 and F_4 (see Figures 6 and 7); the critical time for a tracer output $F(z) > 0.01$ is $t_{\text{crit}} \approx 6.0 \text{ h}$; as F_1 accounts for less than 1% of the overall response, it may be neglected in the numerical evaluation without loss of accuracy.

Sub-reactor $n^\circ F_i(z)$	$F_2(z)$	$F_3(z)$	$F_4(z)$
τ_i in h	13.67	19.14	10.10
Exponent m_i	5.66	2.39	0.77
Effective volume V_i in m^3	41.75	58.42	30.83

furnaces has become a powerful tool in the past 20–30 years to simulate operational conditions in glass melting furnaces, forehearths, regenerators, annealing lehrs, etc. The simple 1-D or 2-D models of glass furnaces initially devised in the 1960s [6] have become fairly complex 3-D simulations whose goals are to interpret furnace operation conditions, evaluate alternate furnace designs, and model different operating combinations for combustion processes and electric boosting (or even all-electric melters). The models yield temperatures within the glass melt, the refractory materials, the combustion space, and even for the exiting glass and waste gases. In addition, they calculate the speed (flow) of glass in the melter and working end and – last but not least – they can deal with glass quality, for instance, in terms of level of defects such as bubbles. Corrosion profiles on the bottom or side walls of the furnace can also be investigated in relation to the directions of glass flow close to the refractory materials [7]. In a word, the major advantage of modeling is to yield a wealth of quantitative information on a working furnace that could not be obtained by any other means.

The theoretical bases of finite-element modeling have been presented in Chapter 1.7. It will thus suffice here to illustrate some application to furnaces from the dog-house to the delivery of the glass to the forming process (see [8–17] for more information). Currently, models may have limitations concerning, for example, glass properties at high melting temperatures and especially processes such as batch charging or furnace corrosion. By their very nature, furnace processes are dynamic so that they are subject to such multi-operational influences that cannot always be modeled. In addition, simulations are of course affected by the uncertainties on their input data for density (Chapter 3.5), gas solubility (Chapter 5.5), and especially for strongly temperature-dependent transport properties (Section 4). Particularly for temperatures and glass flows, the two main operational parameters, in

comparison with actual furnace data are of course playing a basic role in assessments of the validity of models. But none of them are readily measured in industrial settings.

For temperatures, difficulties stem from important gradients, which are typically from 10 to 20 K/cm within the refractory walls, and 3 K/cm vertically. Errors in the positions of the measurements can thus be significant and compound the intrinsic 20 K uncertainties of determinations made with either thermocouples (which are in addition subject to significant drift with time and to radiation in the combustion space) or pyrometers (whose output depend on the assumed melt emissivity and can differ for different wavelengths).

Speed measurements in glass flows are still more difficult. With *floaters* made up of buoyant, inert solids, the speed and direction of motion of the melt are directly monitored. Notwithstanding the difficulty of introducing floaters (for example, through holes in the crown), measurements are made difficult by the narrow field of view of peep holes and their lens distortion, as well as by the forces exerted by the flames, which can be strong enough to move a floater counter to the actual glass flow. As made with strontium or zinc, another technique relies on chemical *tracers* incorporated in the batch whose concentrations are measured as a function of time in the glass produced. Portions of the tracer can reveal the shortest or longest residence time in the furnace whereas the existence of several recirculation loops is indicated by as many concentration peaks. The resolution of the method is limited by 0.5–1 hour uncertainties on the time of the tracer introduction and by the 15 minutes typically elapsing between two analyses, which are significant when the minimum residence time in the furnace is 4 hours.

4.2 The Anatomy of a Furnace

Such tracer experiments are readily simulated with CFD (Chapter 1.7), which yield results that can be accurate to within half an hour [18]. Such a precision is illustrated by residence times in a double convection furnace (Figure 8) where the experimental data interestingly appear to smear out the short-term fluctuations revealed by the simulated results.

Even though companies like Corning and Philips determined glass temperature at depth in melters with special thermocouple techniques, few papers have reported comparisons made between measured and simulated temperature profiles. One such study was early made by Philips in cooperation with the TNO Glass Group (Figure 9) for TV screen melting furnaces [7]. Although the differences between the measured and simulated temperatures could locally reach 30 K, there was already very good agreement between both kinds of data [19].

Of particular importance is of course the circulation of the glass in melters during its chemical homogenization (Figure 10). As described in Chapter 1.7, the process is simulated with the well-known equations of continuum mechanics (e.g. Navier–Stokes, differential temperature, and balances of mass and species) along with the phenomenological laws describing the relationship between flux and gradients (e.g. Newton’s law of viscosity, Fourier’s law of heat conduction, Fick’s laws of diffusion), and appropriate mathematical representations of electric heating, bubbling, and other sources of heat and mass transfer impacting the flow of glass.

These models are usually split in two parts. A primary model calculates temperature and flow in the glass and, separately, combustion and radiation effects whereas a

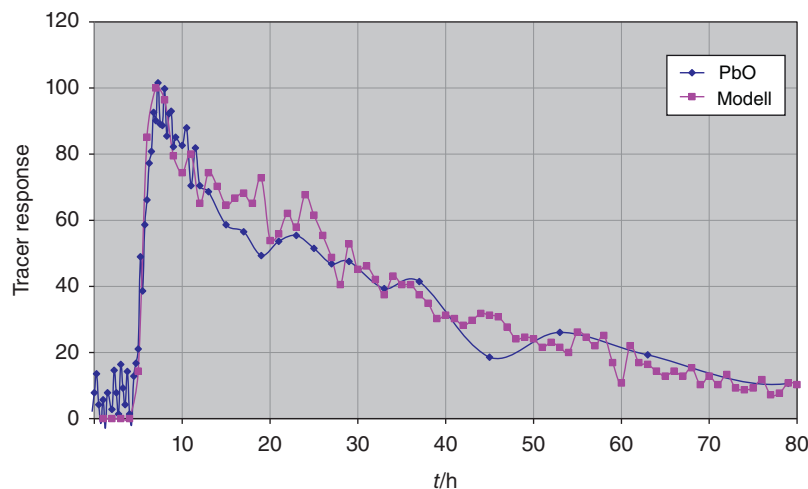


Figure 8 Comparison between tracer residence times in a double-convection furnace measured and calculated by computational fluid dynamics. Long minimum and average residence times of about 10 and 66 hours, respectively.

secondary model takes care of quality by tracing sand grains, bubbles, stones and, in the combustion space, pollutants such as NO_x and SO_x . For a flat-glass melter (Figure 11), an important feature of such simulations is the complex convection pattern whereby part of the melt

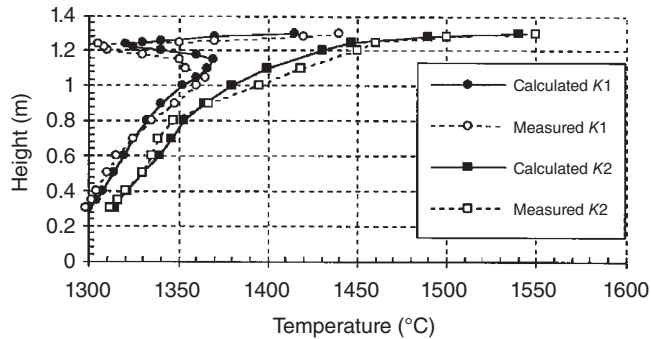


Figure 9 Comparison between calculated and measured temperature profiles for a TV screen melting furnace between its bottom at 0.3 m and the top of melt at 1.3 m [18]. K1 and K2: profiles under the yet unmelted batch and after melting, respectively.

Figure 10 Simplified picture of the glass convection flow within a melter.

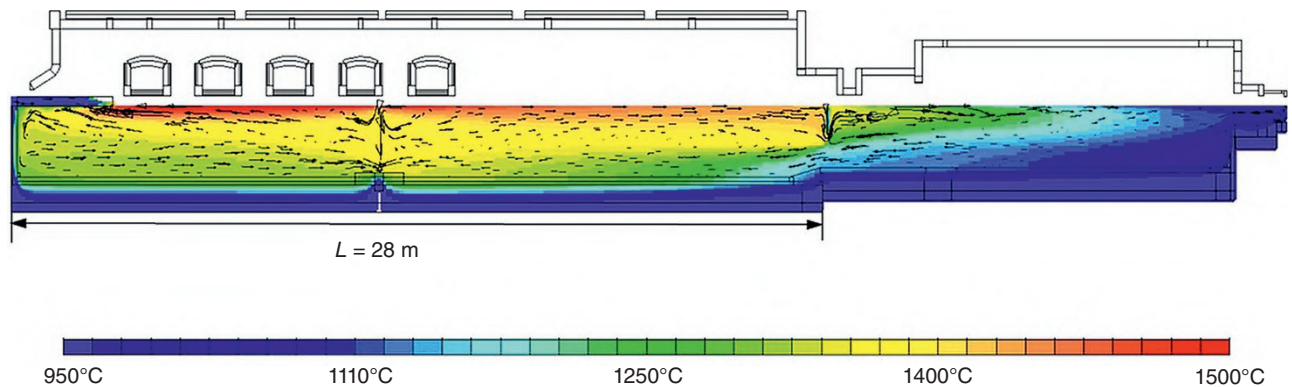
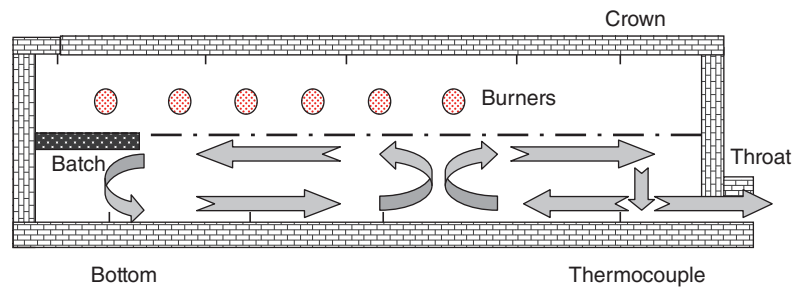


Figure 11 Temperature profiles and melt flow pattern in a flat-glass furnace; recirculation of the melt coming back from the working end on the right-hand side into the melter on the left. Source: Glass Service Co.

comes back from the working end to the melter itself. In more complex simulations, not only the furnace itself but also the associated regenerators may be simulated (Figure 12).

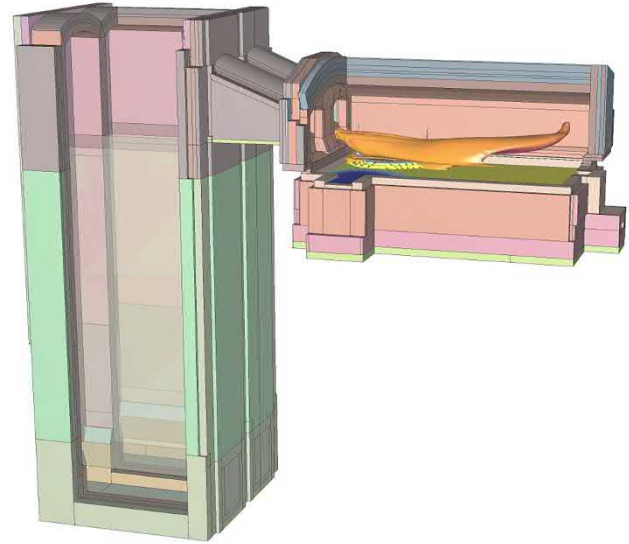


Figure 12 Complete modern furnace simulation model of an end-port, container-glass furnace equipped with a very large regenerator. Source: Glass Service Co.

5 Perspectives

As performed within the Technical Committee 21 of the International Commission on Glass (Chapter 9.12), round-robin tests have been valuable to improve modeling tools to the point that they are now used not only for optimizing furnace design in terms of flexibility, quality requirements, or environmental constraints (Chapter 9.7), but also for controlling on line their operation. But the availability of sound mathematical models should not lead to overlook the act that the real outcome of the simulations also strongly depends on an accurate knowledge of glass properties and the operating conditions of the furnaces themselves. When the relevant glass properties are missing, they must be estimated as reliably as possible whereas all boundary conditions are not necessarily known precisely, for instance, when wall corrosion affects the estimated heat losses.

A major challenge consists in the understanding of the competitive roles of heat transfer versus chemical reaction rate as the limiting step in the batch-to-melt conversion. This competition determines the extension of the batch blanket, which, in turn, has a major impact on the entire process. Conventionally, heat transfer is adopted as limiting step, and chemical turnover is considered to follow instantaneously. Depending on the type of batch as well as on the stage of reaction progress, however, chemical turnover may be in control. Understanding this issue would enhance the possibility to predict the extension of the batch blanket in a more reliable way.

Appendix

Solution to the system of Eqs. (15a)–(15d)

The flux q_{ht} is given by

$$q_{ht} = q_2 - q_1 = \sigma \cdot \left[\varepsilon_{\text{gas-melt}} \cdot (T_{\text{gas}}^4 - T_{\text{melt}}^4) + \varepsilon_{\text{crown-melt}} \cdot (T_{\text{gas}}^4 - T_{\text{melt}}^4) \right].$$

The effective emissivity coefficients for radiative heat exchange between gas and melt, and crown and melt, respectively, are the following expressions:

$$\varepsilon_{\text{gas-melt}} = \frac{\varepsilon_{\text{gas}} \cdot \varepsilon_{\text{melt}} \cdot (2 - \varepsilon_{\text{gas}} - \varepsilon_{\text{crown}} + \varepsilon_{\text{gas}} \cdot \varepsilon_{\text{crown}})}{1 - (1 - \varepsilon_{\text{gas}})^2 \cdot (1 - \varepsilon_{\text{crown}}) \cdot (1 - \varepsilon_{\text{melt}})},$$

$$\varepsilon_{\text{crown-melt}} = \frac{\varepsilon_{\text{melt}} \cdot \varepsilon_{\text{crown}} \cdot (1 - \varepsilon_{\text{gas}})}{1 - (1 - \varepsilon_{\text{gas}})^2 \cdot (1 - \varepsilon_{\text{crown}}) \cdot (1 - \varepsilon_{\text{melt}})}.$$

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9.9

Glass Cullet: Sources, Uses, and Environmental Benefits

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1 Introduction

Glass is one of the more common materials in daily life. It is used in glass containers for food and beverages (Chapter 1.5), windows for buildings (Chapter 9.1) and all kinds of vehicles (Chapter 9.2), fibers for insulation (Chapter 9.3), continuous fibers for reinforcement (Chapter 1.6), screens of electronic displays (Chapter 6.10), household products, etc. Among a great many other advantages, it can be considered to be a “permanent material” [1] as it can in principle be recycled indefinitely to produce new glass without significant loss of material, which means that 1 kg of small glass fragments called cullet can be melted to produce 1 kg of new glass. This feature makes glass one of the best materials for the development of the circular economy concept with a low consumption of new raw materials and a reduced exploitation of natural resources.

In 2007, the world glass production was estimated to be 115 million tons, the European Union (EU) representing 32 % of the total [2]. The global market for container glass packaging accounted for 46 million tons in 2012 [3] and for flat glass (buildings, automotive mainly) for 52 million tons in 2009 [4], thus representing together almost 85 % of the worldwide production. The remaining 15 % went to the production of tableware, glass wool, continuous fibers, and specialty glass. Such data are estimates and should be taken with caution because other reports provide different figures. But such differences do not matter at all for the purpose of this chapter, which is to deal with the environmental issues raised by these large quantities, particularly in terms of waste management.

In this respect, the hierarchy of options for waste disposal (Figure 1) set by the Waste Framework Directive 2008/98/EU [5] must be taken into account. Any option depends on financial, social, and environmental considerations; for glass, however, it is well accepted that reducing the production of waste while increasing reuse and recycling should be the preferred option. But if reuse is a priori considered to be the best option from an environmental point of view, it is facing real limitations caused by the difficulty of implementing it in practice. The reuse of empty containers is, for instance, economically and environmentally advantageous only if both product and brand are part of a local market, as is the case of local milk or beer distributors. But it is not viable when products either have long end of life, as is the case of windows for building, windmills, etc., or cover global-, national-, or regional-scale production as in the wine, beer, mineral water, food, or automotive industries.

In contrast, the recycling or recovery of glass after transformation into cullet can potentially be applied everywhere for the production of new articles. In such cases the end-of-life glass pieces need to be collected and delivered in specialized facilities to be treated through grinding, cleaning, sorting, etc., before being supplied to glassmakers. The key advantages of recycling or recovery is the reduction of waste disposed or dispersed as litter, as well as the reintroduction of secondary materials back into the economy.

The sources of recovered glass for glass recycling mainly come from container glass packaging and flat glass, as they account for the majority of glass produced worldwide and are relatively uniform in terms of composition, being constituted by soda-lime-silica glass. The present chapter will thus focus mainly on glass cullet recycled from these sectors. The different categories of cullet will be first presented. The problems raised by glass recycling will then be briefly reviewed. Following a

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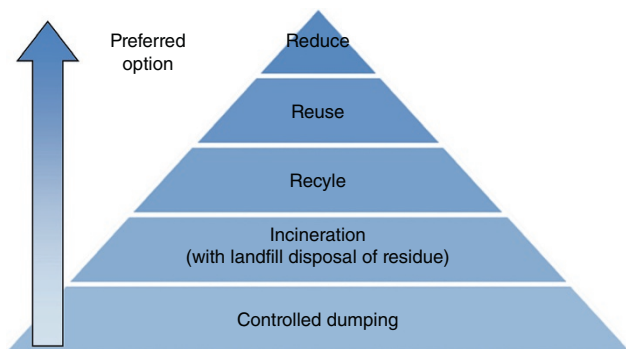


Figure 1 Hierarchy for glass waste.

discussion of the current cullet sorting technologies, the nature of the rejects, their disposal, and the environmental benefits of recycling will finally be discussed.

2 Basic Features of Cullet

2.1 Categories

Cullet depends on the type of industry considered and on the availability of a collecting and reprocessing system. Its sources can be either rejects produced during manufacturing of flat or container glass, continuous fibers, glass wool, special glass, tableware, etc., or end-of-life articles such as bottle and jar containers, TV screen, windows, automotive glass, tableware, etc.

In spite of this diversity, glass cullet can nonetheless be split in two main categories depending on its source. The *internal* cullet is mainly composed of defective products rejected during the manufacturing process as a result of quality control, transition between two different kinds of production (color change, parameter modifications, etc.), or secondary process rejections (cutting, grinding, etc.). As to the *external* cullet, it is waste glass collected and/or reprocessed with the purpose of recovery or recycling.

External cullet can itself be divided further in two types:

(i) *Pre-consumer* (industrial) cullet resulting from the manufacturing of glass products, which is not internally recycled and leaves the facility as waste; this material can be recycled in another facility for the production of glass, reused for other specific applications (such as road filler, aggregate, etc.), or disposed in landfill.

(ii) *Post-consumer* cullet, produced from glass products originating in the consumer market, including glass bottles, jars, tableware, windows, vehicle glazing, etc.; this material can be recycled into new products after appropriate collection and treatment process and/or reused

for different purpose than production of new glass, for example, as road or aggregate filler.

The relative amounts of pre- and post-consumer cullet vary considerably depending on the industrial structure and waste policy in place in the specific country. The latter cullet nonetheless predominates, especially where a collection and recovery system is available, followed by flat glass pre-consumer cullet. Reflecting much the much lower quantities produced, the smallest amounts are pre-consumer glass cullet from mineral wool, continuous filament fiber, special glasses, etc.

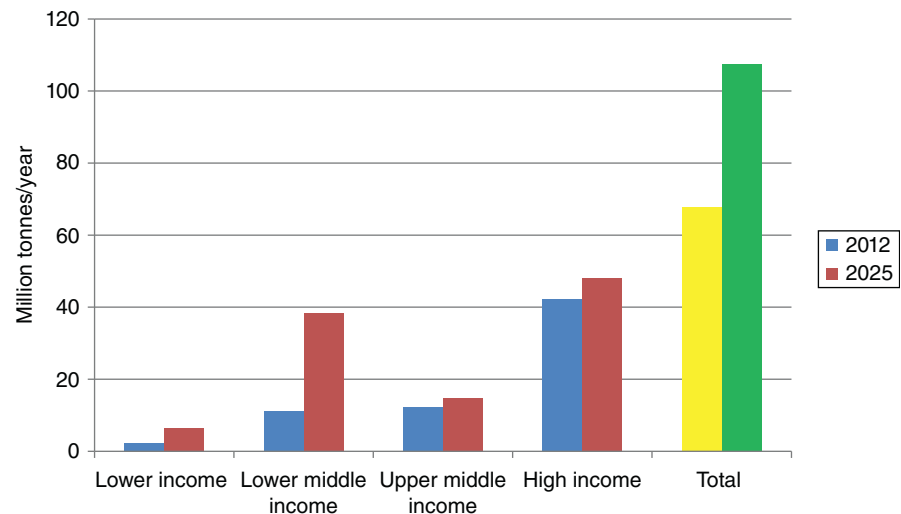
2.2 Glass Waste: Some Comparisons

Municipal solid waste (MSW) is locally determined by the degree of development and industrialization, energy sources, climate, and also social and cultural behavior as documented by a World Bank report that illustrates the variability of its generation and composition [6]. It comes as no surprise that the amount of MSW generated per capita is higher in developed countries and urbanized areas where the proportion of man-made materials such as plastics, glass, and aluminum is in addition higher in comparison with biogenic products such as food or garden and wood waste. The same World Bank report gives data from which the increase of waste glass from 2012 to 2025 in MSW can be estimated for four categories of countries grouped according to their relative wealth (Figure 2): lower income (Vietnam, Serbia, Ethiopia, etc.), lower middle income (China, India, Turkey, etc.), upper middle income (Uruguay, South Africa, Mexico, etc.), and high income (United States, Germany, Japan, etc.) [6].

Although global estimates have been made for the production of waste glass, analogous figures are lacking for current or projected rates of recovery worldwide. As representative examples of two widely different systems, Europe and the United States will be selected here to contrast a high/low recycling rate along with a well-established/developing policy for glass waste collection and recycling. In preamble, however, it should be noted that high reuse or recycling glass rates can also obtain in countries lacking specific environmental policy or collection systems. In many developing countries, informal waste pickers at collection points and disposal sites recover indeed a significant portion of discards.

A specific legislation has constrained member countries of the EU to adopt policies for the collection, treatment, and recovery of packaging waste [2]. It specified a target of 60 % cullet recycling by 2008, which is actually to be increased to 85 % by 2030. As a result, Europe probably is the region with the highest recycling rate for glass. As

Figure 2 Estimation of waste glass generated by municipal solid waste.



split into six different sectors, the amounts of glass produced and of waste generated, collected, and recycled are listed in Table 1. Of this waste, pre- and post-consumer cullet represent 25 and 75 %, respectively [7]. For container glass the data of Table 1 mainly refer to post-consumer waste, whereas the opposite holds true for flat glass and tableware. As for the amount of cullet collected and recycled from mineral wool and continuous fibers, it is negligible compared with that of container glass.

Post-consumer container glass thus is the main source collected, processed, and recycled to produce new container glass for the food and beverage industries. The proportion of recycled container glass nonetheless remains strongly impacted by national waste legislations as illustrated in Table 2 where the EU-28 recycling rate in 2014,

Table 1 2007 European statistics for glass cullet. End-of-waste (EoW) criteria for technical proposals (million tons) [7]. Figures expressed in Million of tonnes.

Glass sector	EU production	Waste glass generated	Waste glass collected	Waste glass recycled
Container glass	21	17	11	8
Flat glass	9.5	5.1	2.9	2.9
Tableware	1.5	0.8	0.5	0.5
Mineral wool	3.7	2	NA	NA
Continuous filament fiber	0.7	0.4	NA	NA
Special glass	1	0.5	0.45	0.4

calculated as the ratio between the total amounts of glass recycled and collected, varies from 21 % (Greece) to 102% (Sweden). The average value is 74 % (70% if Turkey, Norway, and Switzerland are included), seven countries having already outdone the 2030 target of 85 %, namely, Austria, Belgium, Denmark, Germany, Luxembourg, Slovenia, and Sweden (or nine if Norway and Slovenia are included). Potentially higher quantities of post-consumer cullet could be recovered from end-of-life vehicles (ELVs), electrical and electronic equipment, and building demolition. Such materials are not yet well regulated in Europe, however, and the recycling industry is still facing cost issues related to the collecting system and quality of the final materials.

Estimates of the total amount of glass produced in 2013 in the United States and of the relative amounts recovered and discarded are listed in Table 3 [8]. Although the amount of glass containers recovered from MSW increased from 2.6 to 3.2 million tons between 2005 and 2013, it represents a fraction of only 27 % of the total glass made and 34 % of the container and glass packaging produced. Compared with those mentioned for the EU, these numbers are thus very low even though the notion that glass is a recyclable material is well established in the United States where there is widespread access to glass recycling and where the recovered cullet is used to make new glass containers and other products such as insulating fibers or aggregates for drainage and roadbed applications. This contrast is readily explained in terms of differences in infrastructures and public policies: whereas landfill costs are much lower in the United States, distances to remanufacturers are longer, and collection systems are not subsidized by industrial consortiums.

Table 2 2014 EU-28 recycling rates.

Country	National consumption (tons)	Collection for recycling (tons)	%
Austria	263.700	233.700	89
Belgium	324.579	305.118	94
Bulgaria	78.251	49.434	63
Czech Republic	189.542	135.697	72
Cyprus	18.947	6.081	32
Denmark	159.712	135.642	85
Estonia	41.128	29.939	73
Finland	77.090	62.720	81
France	2.705.000	2.000.000	74
Germany	2.748.300	2.445.500	89
Greece	96.000	19.867	21
Hungary	96.680	35.068	36
Ireland	155.347	119.683	77
Italy	2.298.500	1.764.000	77
Latvia	54.090	29.790	55
Lithuania	66.545	36.434	55
Luxembourg	29.435	27.891	95
Malta	10.279	5.049	49
Netherlands	533.000	427.000	80
Poland	1.060.588	623.122	59
Portugal	363.762	199.010	55
Romania	167.169	66.129	40
Slovak Republic	157.268	61.256	39
Slovenia	32.982	28.319	86
Spain	1.391.000	953.100	69
Sweden	193.502	197.093	102
United Kingdom	2.399.000	1.612.762	67
Croatia	76.590	40.261	53
Total EU-28	15.787.986	11.649.665	74
Norway	65.737	62.063	94
Switzerland	371.148	357.568	96
Turkey	1.196.213	167.276	14
Total Europe	17.421.084	12.236.572	70

2.3 Cullet Applications

The possible uses of pre- and post-consumer cullet from different sources are many although the proportion of recycled material can be really high only for containers and insulating fibers (Table 4). Among the main glass products, containers are in general those for which raw material requirements are the less stringent and for which production costs must be as low as possible to face a stiff

Table 3 Glass recovered and discarded in 2013 in the United States. Figures expressed in Thousand of tonnes.

Glass sector	Production	Recovery	Discard
Durable goods (furniture, appliances, electronics, etc.)	2280	Negligible	2280
Glass containers	9260	3150	6110
Total glass	11 540	3150	8390

competition from other materials such as plastics or aluminum. The majority of the cullet recovered is thus recycled into new colored glass containers. In Europe, some manufacturers are even able to use more than 90 % of mixed colored and colorless cullet. Production of colorless containers is in contrast limited because high-quality cullet has to be supplied either by distinct collecting systems or by secondary color sorting processes. Likewise, the proportion of cullet from external sources used to make flat glass is as low as possible in view of the color stability and lack of defects required. Some experiments are nonetheless made in Europe to produce flat glass using 30% of recycled clear, low-iron glass.

Recycling of cullet is impacted at the national level not only by specific legislation imposing a recycling rate target but also by the availability of supply chains providing glassmakers with a continuous delivery of cullet at an acceptable quality and cost. When such system are not available, or the cost of cullet is higher than that of the mineral batch to be replaced, other secondary market applications for glass cullet have to be found. In general, these do not require as strict quality criteria as for glass-making. Cullet then becomes less expensive than usual raw mineral materials for making abrasives or ceramic sanitary ware, fluxing agents in brick manufacture, or fillers in water-filtration media and in civil works.

3 Glass Recycling

3.1 Container Glass

Pre-consumer cullet can be collected directly from the producing plant. At the country level, specific legislations define what waste is and the procedures to be followed accordingly. Post-consumer cullet can be collected in two main ways, either as glass only in the so-called bottle banks or otherwise as glass mixed with other dry recyclables such as metals and plastics. Mono- and multi-material collection systems have their own advantages and drawbacks. Especially when glasses of different colors are collected separately, mono-material systems provide a higher-quality cullet with a lower fraction of impurities.

Table 4 Origin and possible applications for cullet.

Origin of the cullet	Possible application	Potential range of recycling
Container glass, glass packaging	• Container glass (excluding flaconnage, borosilicate container, and high-quality tableware)	20–90 %
Flat glass	• Insulation mineral wool • Container glass • Flat glass	10–40 % 20–90 % (mainly colorless glass) 20–30 %
Insulation mineral wool	• Insulation mineral wool	20–60 %
Continuous filament glass fiber	• Continuous filament glass fiber	10–30 %
Tableware	• Container glass (excluding lead crystal glasses) • Tableware • Insulation mineral wool	20–90 % 10–20 % internal cullet 20–60 %

Table 5 Scrap from mono-material collection in bottle banks (unpublished SSV data).

	Percent of material	Percent of rejected stream after treatment	Percent of glass lost in the different stream
Metals	0.6	0.9	0.3
Waste	1	1.9	0.9
Ceramics	0.15	3	2.85
Glass	98.25	94.2	
Total	100	100	4.05

Table 6 Scrap from multi-material collection in bottle banks (unpublished SSV data).

	Percent of material	Percent of rejected stream after treatment	Percent of glass lost in the different stream
Metals	5.6	7.4	1.8
Waste	19.4	25.1	4.1
Ceramics	2.2	20.3	18.1
Glass	72.8	47.2	
Total	100	100	25.6

Typically the proportions of rejects, i.e. non-recyclable residues present in the collected material, are 1 and 12–15 % for mono- and multi-material collection systems, respectively. But the former are more costly than the latter, especially if color separation has to be made, and are more complex to manage for households in terms of both handling and sorting space.

Estimates of the amounts of scrap mixed with glass have been made for both mono- and multi-material collection systems (Tables 5 and 6). The values represent only rough estimates as they strongly depend on the willingness of the citizens to follow the recycling rules and on the posttreatment process applied to separate the different materials and to remove impurities. The figures nonetheless show that in multi-material collection the amount of cullet lost with the other materials (metal, waste, and opaque bodies) is definitely higher, reaching 26% of the total input.

3.2 Flat Glass

Almost 80% of flat glass is used for building application, 15% for vehicle glazing, and the rest for other purposes [9]. In any country recycling of flat glass is thus strongly

impacted by the existence of specific environmental policies and, in particular, of legislation on construction and demolition (C&D) waste and/or ELVs to be implemented in recycling programs.

Although flat glass currently represents only 0.4% of C&D waste [10], this value is expected to increase through the increasing use of glass as a structural element in architecture (Chapter 9.1). That flat glass is such an insignificant part of a building makes of course its recycling especially difficult given that the removal of glass panels prior to demolition is not economically viable. Flat glass is thus absorbed into other streams, so its amounts recovered from C&D remain low. But new regulations are under discussion worldwide to promote its recovery and produce cullet for different applications.

For ELVs the dismantling processes focus on the recovered metal, which accounts for 75 % of a car mass. Glass represents only 3%, the remaining 22 % being a complex heterogeneous waste that contains many different plastics (thermoplastics and thermosets), elastomers, foams, remaining metals, wood, or textiles. Recycling of such a heterogeneous stream is currently neither technically nor economically feasible, so landfilling prevails. Again, national policies will be enacted to recover more material.

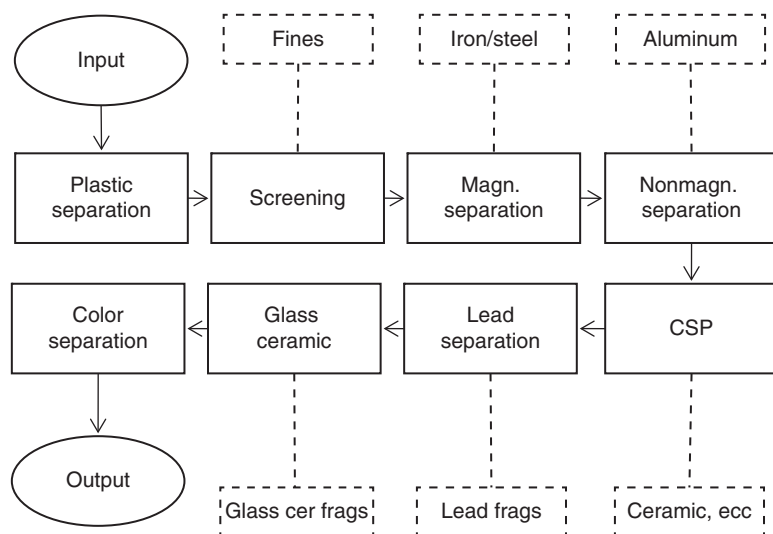


Figure 3 Cullet treatment process. CSP, rejects of ceramic, stones, and porcelain.

As for glass, its removal before shredding will then be mandatory as cullet cannot be recycled once contaminated with metal scrap.

4 Separation Technologies

4.1 Treatment Systems

Prerequisites to obtain a stable, clean, and ready-to-furnace cullet are (i) to avoid the presence of all possible polluting materials harmful for the final glass container such as ceramics, stones, glass ceramics, and metals, (ii) to eliminate fragments of lead crystal glass, (iii) to achieve a sharp grain size distribution limiting the volume fraction of fines, and (iv) to eliminate organic materials such as paper, wood, and plastics. If fulfilled, these conditions imply that the cullet is no longer waste but a true secondary raw material. In practice, the details of the process may vary from one setup to another. The sketch of Figure 3 is only a general description of one possible process designed to clean cullet. For some companies the order of the operation can vary, depending on the type of incoming material and internal business decision.

The input material comes from municipal waste dry recyclable. The output can be either mixed cullet or flint (colorless glass) cullet produced by color separation plus the remaining cullet that have been separated from the flint. In fact color separation is usually applied to mixed cullet to get white (colorless) or half-white cullet, whereas the rest is a mixed cullet with a lower flint fraction. If managed correctly, the treatment results in a final mixed cullet product that is virtually clean from ceramic, stone, plastic, and metallic contaminants (Figure 4).

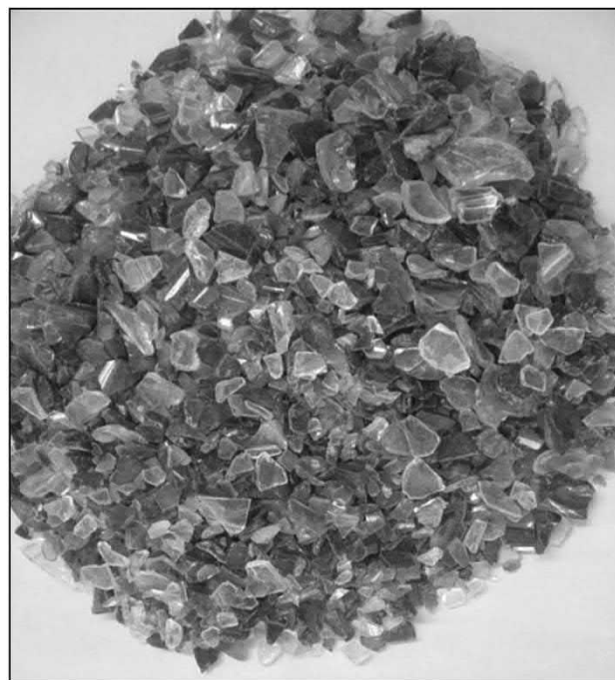


Figure 4 Mixed glass cullet.

4.2 Sorting Machines

Different detection systems are used to remove the fragments of undesirable contaminants. Broadly speaking, there are four types of such systems: (i) visible near-infrared detection [11] to remove glass ceramics, (ii) visible light detection to remove opaque material (CSP) or to separate colors, (iii) UV fluorescence detection for the removal of lead-glass fragments, and (iv) X-ray fluorescence detection for the removal of

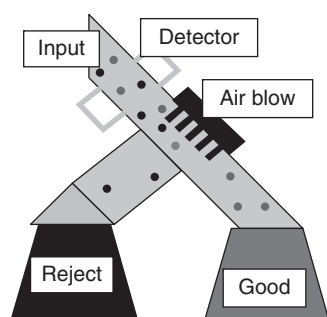


Figure 5 Sketch of a typical sorting machine for cullet.

material with a specific composition, especially useful for lead-glass fragments.

These machines in general work continuously by letting the cullet flow through the detection system, which triggers a subsequent array of air blows that are activated when some contaminating material is identified (Figure 5). Actually even the highest-quality cullet is not completely free from contaminants because various factors make the efficiency of removal of these machines lower than 100 %. These are (i) the condition of material because the ability of a system to recognize an undesired material depends on cleanliness of the glass (and, thus, on surface humidity or on the amount of contaminant attached to the fragment); (ii) the type of material because the waste is not always processed at the same rate and may come from different places and because the sorting machine must be calibrated accordingly as the quantity and nature of the contaminants can differ; (iii) the air blow, which is not selective and does not remove only the undesired contaminant, but also neighboring glass fragments; and (iv) the stream effect, caused by the fact that the air blow is not instantaneous but has a certain finite duration so that other fragments in the tail of the target can be erroneously removed even with the best synchronization. Because of these effects, the rejected material can thus contain “good” glass, whereas the clean glass can still contain some contaminants.

4.3 Rejects

All operations applied to clean out multi-material to obtain glass cullet necessarily yield a certain amount of rejects, which still contain a certain amount of “good” glass. Hence, it is useful to describe also briefly the various types of rejects and then to review possible strategies for recycling of rejects according to the appropriate workflow (Figure 3).

Organics comprises paper, wood, and plastic (hard and soft package), along with residues of adhesives (for labels), sealants (PVB, rubber), oil, and grease. Depending on the

type of glass to be recycled, these are taken out differently. If color separation is included in the workflow, sealants (e.g. PVB, rubber) are eliminated by dry methods only for the flow of half-white glass [12].

Small pieces of paper, fragments of wood, fabrics, residues of adhesives, sticking oils, and greases are rarely washed out but simply burned at a suitable temperature (about 600 °C). Big plastic pieces are often taken out by visual and manual sorting, whereas small, loose fragments are usually eliminated together with glass fines by sieving.

Scrap of metals such as iron, steel, and aluminum are taken out from multi-material waste in several steps. Often the material delivered to the collection sites is pretreated with magnets and electrostatic systems to take out big pieces of magnetic metals and aluminum cans, respectively, with the added advantage that aluminum is itself another valuable recyclable for the metal industry. After this pretreatment the material is more suitable to be processed by sorting machines. During this subsequent flow, a second round of magnetic and nonmagnetic separation is performed to remove metallic contaminants as much as possible. This material is usually sent to companies possessing a technology suitable for waste metal processing so as to provide clean metal scrap to be reused for metal processing.

Ceramics, stones, and porcelain (CSP) designate all inorganic contaminants that cannot be melted in a glass furnace, such as pieces of fireclay, rocks, bricks, and ceramic and porcelain fragments erroneously discarded in the multi-material collection bins. If present in a glass batch, these materials may melt incompletely in which case they give rise to *stones* (Chapter 1.2), which are a cause of rejection of the glass produced (Chapter 1.2). These refractory contaminants are thus usually removed with optical sorting systems that discard opaque fragments and clear out the cullet flow. The reject usually contains a large quantity of glass, which is unfortunately lost in the workflow if a recovery strategy is lacking.

Glass ceramics often comes from cookware, dismantled oven windows, and cooktops. These materials are hardly distinguishable from normal glass, and the technology of sorting, even if it is already applied to the treatment workflow, is not as mature as the others.

Fines are usually removed from the workflow first through sieving of the pretreated material at some size cut to facilitate the removal of glass contaminants by the sorting machines. This size is determined by the efficiency of the sorting machine itself, which actually can work from 5 to 8 mm size upward. Below this size, the removal of CSP contaminants at the required quality level cannot be guaranteed with the removal efficiency of the most widely used technology.

4.4 The Particular Case of Lead Glass

There are different forms of legislation in place, as example in the EU as well as in the United States, which set specific limits for heavy metals (mercury, cadmium, lead, and chromium IV) in packaging and packaging waste. The amount of mercury, cadmium, and chromium IV in glass containers is negligible because these elements are present neither in the raw materials nor in the glass cullet recycled. However, lead can be detectable as it can be introduced in the glass furnace through the cullet stream, which can contain small amount of crystal glass fragments recycled together with the soda-lime-silica glass containers. To be in compliance with the specific legislations, the removal of lead-glass fragments is mandatory, especially when the recycling rate is quite high.

Lead-glass fragments are mostly scrap glass from cathode-ray tubes (Chapter 6.10) mixed with small amounts of tableware crystal glass. Because EU regulations have set an upper concentration of 200 ppm Pb in glass, efforts have been made to develop technologies for sorting out lead-glass fragments from the cullet workflow. But some cullet is inevitably rejected along with lead fragments and is lost as it is usually sent to a suitable hazardous waste dump. Great care must be taken in cullet cleanliness as well, since a fragment of polluting lead glass may not be removed from the stream if it is not recognized by the sorting detector, as it might happen when the glass fragments is covered by mud.

The lead content of rejected lead glass is so high that its direct reuse in glass industry is not advisable. Different processes are potentially applicable to dispose of them, but they are in general not economically sustainable. A chemical process devised [13] to recover a material possibly suitable for the glass industry and other types of production involves the solubilization of the glass scraps in a caustic environment (NaOH) and the separation of metallic lead with an electrochemical cell. The solution is then treated to recover the sodium silicate and possibly to reuse also the insoluble silicate (of Ca, Mg, etc.) in the glass industry. The process has been devised for CRT scrap glass whose PbO content is about 30 wt %. But the economic viability of this process remains to be assessed for the sorting-machine cullet whose PbO content is about one order of magnitude lower.

4.5 Reject Minimization

The fraction of rejects generated depends on the type of material processed, the condition of the material (presence of mud, water, paper), and the final quality desired. In this respect, the upstream cleaning steps of plastic,

scrap-metal and fines removal, organics burning, and washing are most important to optimize the efficiency of the downstream sorting machines and, thus, to minimize the improper rejection of cullet and the amount of waste to be landfilled. The sorting technology can by itself make a difference. The efficiency of these machines is related to the flow rate, the cleanliness of incoming cullet stream, and the dimensions of the fragments to be removed. As actually applied in the most modern treatment plants, average flow rates of about 20 tons per hour give a consistent stream of processed cullet to feed the glass container industry. In this situation the sorting machine could reject a certain quantity of “good” cullet through the jet stream effect, lowering the recycling yield of the treatment plant and, in consequence, that of the overall treatment system.

The minimization strategy in this case relies on multi-blow arrays and short blow pulses to reduce the jet stream effect and, thus, the reject of good cullet. Dirty cullet would cause false-positive reject, that is, a glass fragment could be recognized as pollutant to the sorting machine, in the case of CSP removal (opaque appearance). For UV sorting of lead glass, the presence of pieces of paper on the fragments could cause the reject as paper is usually active under UV light. In this case the minimization strategy mainly relies on the cleanliness of the incoming cullet stream, which depends on the initial condition of the material and on the efficiency of the operations performed upstream.

5 Miscellaneous

5.1 Cullet Quality

Nowadays cullet is widely used in the container glass industry thanks to its beneficial effect on environment and process economy. These benefits were and actually are the driving force for the continuous improvement of the quality of the collection and treatment systems. Good cullet available to the glass container industry leads to a high efficiency (low rejects, low added costs) and a high quality in terms of both added value and color matching and stability, for which the demands of bottling and packaging firms are stringent.

Good cullet comes from up-to-date and efficient treatment plants, which apply the most modern technologies for sorting and the most efficient strategy for the recovery of rejects. In addition, the efficiency relies also on the type of input material: the collection system could be multi-material (glass, plastic, and metals), single material (glass only), or even color separated.

5.2 Redox and Color

Even under the most favorable conditions, cullet carries residues of sticking papers, glue, oil, and grease. With average utilization levels of about 60–65 wt % of the total batch and peaks of 90–95%, a 0.5 wt % organic content could be detrimental for the melting kinetics in the furnace and color stability of the glass produced. Acting as reducing agents, organics change the redox state of the melt and, thus, the equilibrium between Fe^{2+} and Fe^{3+} that determines glass color (Chapter 6.2), giving rise to quality problems when causing deviations from the optimum range. In addition, the melting kinetics of the batch may slow down as a result of foaming in the furnace (Chapter 1.1), whereas the presence of bubbles or stones leads to an increase of rejection rates.

The introduction of color sorting machines has had a positive impact on the amount of cullet recycled, but some unexpected contraindications have been noted. The redox [14] state of the cullet fed depends on the relative amounts of the different colors. Usual mixed cullet containing flint glass is no longer widely available on the market, and the colored cullet obtained after flint cullet separation is a mixture of green and amber. This change in composition and color leads to a different product. When used for the production of colored glass, small variation, for example, can modify the batch redox number (a measure of its reducing power; cf. Chapter 1.3, [15]), causing color instability, especially for reduced glass such as amber and UV absorption glass (UVAG).

5.3 Possible Reject Valorization

Valorization of rejects must be evaluated in the analysis of the type of contaminant that could harm the final product, the glass container. Different types of reject require different recovery strategies. As an example, CSP fragments of more than 8 mm in size cannot be digested completely in a glass furnace (Chapters 1.2 and 1.3), which is in about 20 hours of melting at about 1450 °C. Their remains are then found as stones in the final glass containers, which are discarded by the in-line control before palletizing. A possible strategy for the recycling of CSP for glass container production is grinding, whereby fragments reduced to a size millimeter are easily digested by the melting furnace. This fine material obtained from grinding of CSP rejects and often fines is called glassy sand. To produce it the CSP reject is usually cleaned from very big fragments of material still present, mixed to the fine fraction, eliminated upstream, and grinded together with a lower granulometric profile.

Another possible use for CSP and fines reject is as road substrate, especially for grain sizes lower than 2.36 mm

[16]. Coarser sizes do not give the appropriate shear strength, which make these rejects unsuitable for geotechnical engineering applications. Other possible uses of fine-grained cullet reject currently under study concern cement, fireclay, and concrete.

6 Environmental Aspects

6.1 Cullet Life Cycle in the Light of Circular Economy Concept

In recent years policy makers have been increasingly involved in defining strategies and political and legal actions to implement and enforce the concepts of sustainable development and circular economy. The goal is to ensure a safer future where the challenges of resource scarcity, environment pollution, climate change, etc., can be kept under control or even overcome. Within this framework, a “responsible” management of resources is promoted through minimization of the waste streams sent to landfill disposal and incineration and preferential usage of resources that are effectively renewable or indefinitely recyclable over time.

As already stressed, glass is one of the best materials in terms of circular economy as it can be considered as a *permanent material*, which can be theoretically recycled an infinite number of times to manufacture a new glass article without significant addition of mineral raw materials. The percentage of glass cullet substituting mineral raw materials can reach up to 95% of the total bath composition. The main issue for such target is the availability of an efficient collection system, cullet treatment process, and market.

6.2 Environmental Benefits

Given a typical batch composition for a soda-lime-silica glass (61.9 wt % silica sand, 17.8 soda, 11.3 marble, 5.5 dolomite, 1.8 feldspar, and 1.7 others), one readily estimates that 1.2 tons of raw materials is saved per ton of recycled cullet used. Out of this 200 kg difference, about 150–160 kg represents the amount of CO_2 released upon heating and melting by carbonate raw materials such as soda, marble, or dolomite (the remaining weight is the water added or present in the batch and small amount of sulfates and organics). In addition, less energy is needed to remelt cullet than to melt a batch of raw materials. The difference amounts to 2.5 % of the total glass-melting energy consumption for each 10 % cullet added to the batch [17].

Besides, the use of cullet allows significant savings in terms of the “indirect” energy spent for the extraction,

production, and transportation of raw minerals. When the energy needed for the collection, treatment, and transportation of cullet is also taken into account, the net benefit is also clear although it of course depends on the assumed energy consumption for the extraction and production of the raw materials, on the origin and distribution of this energy, and on the type of system adopted (i.e. gate to gate, cradle to gate, cradle to grave, or cradle to cradle). For the most significant cradle-to-cradle case, a comprehensive life-cycle assessment (LCA) has been made by FEVE [18], the European Container Glass Federation, together with GPI, the US container glass trade body. For a whole cycle returning a container to its original condition after use, the result is that one ton of recycled cullet gives rise to a saving of 670 kg of CO₂ by comparison with the use of extracted raw materials.

The use of cullet thus translates into considerable environmental advantages in terms of reduced consumption of mineral resources, less intensive mining activity, lighter CO₂ footprint, lower energy consumption, and reduced amounts of materials to landfill or incinerated. And these advantages are especially noteworthy as glass can be recycled indefinitely.

7 Perspectives

Beyond the Paris Agreement and incentives for sustainable development, the main commitment in the future would be the limitation of the use of natural resources and the lowering and containment of CO₂ emission. For sectors with high energy and CO₂ footprint such as the glass industry, there is no choice but to continue and to increase the use of recycled glass: these goals can be reached by a strong, common commitment of the different entities involved in the circular economic frame of glass.

The glass industry must improve the technological control of the process, being able to cope in almost real time to possible fluctuations in cullet quality and to increase the use of secondary raw material obtained from the cullet reject valorization. Treatment plant must apply the best reference techniques for glass cleaning and sorting and find strategy for convenient process design. Citizens must be aware of the impact of their waste, being responsible on the destination of possible recyclable material. Authorities must give definite leverage to industry for making investment for coherent innovation possible toward a more closed and sustainable circular economy and by making these goals known to the general public.

An increasing use of cullet in the whole developed world is unlikely given the already high level of recycling.

Probably only in the United States and Russia is there room for consistent growth if suitable actions are undertaken to activate a sustainable system. But developing countries, as well as BRICS, should from the beginning apply the best practices to limit the overall environmental impact of their growing economies.

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9.10

Immobilization of Municipal and Industrial Waste

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1 Introduction

Waste disposal is an issue as old as urban life. With the invention of the city in Mesopotamia more than five millennia ago, not only did waste become spatially concentrated through marked increases in population density, but the economic growth made possible by the division of labor caused the amount of waste produced to rise correspondingly. By far the simplest way to dispose of garbage long remained to throw it away, hence the regular elevation of the ground surface observed in many old cities. If such practices have since then proved a boon for archaeologists thanks to the great many artifacts (glass and ceramics, in particular) that can be recovered underground, the need to limit garbage accumulation was recognized early. To reduce the filthy smell of the Parisian mud stirred by horse carriages, the French king Philip August (r. 1180–1223), for instance, ordered in 1184 the streets of the city to be paved with “hard and resistant cobblestone,” a decision that none of his predecessors had taken because of the difficulty and high cost of the work [1]. But it would take a very long time before garbage became actually collected so that in the eighteenth century chroniclers were still complaining about the dirtiness of European cities. This awareness was enhanced in the nineteenth century through recurring episodes of epidemics like cholera and understanding of their microbiological causes. Although waste began to be regularly collected, it was in general simply dumped in growing volumes at the outskirts of the expanding cities.

Toward the end of the nineteenth century, the idea to incinerate waste was thus formulated to reduce its volume by 90 % and to eliminate safely any disease-carrying agents. The first municipal waste incinerator (MWI) was installed in Nottingham (England) in 1874. From 1887 to 1908, about 200 incineration plants were constructed in Europe in spite of the resistance met among local people because of bad smell and dust production. When water-steam networks were developed in the late nineteenth century, garbage became one of the energy sources exploited, but cheap energy and concerns about emitted pollutants later on caused operation of incineration plants to meet with difficulties. In the 1970s, the issue came back to the fore as a result of the energy crisis, so new municipal waste combustion plants were built to produce heat for the generation of steam and/or electricity. At the same time strict regulations were enacted to limit the emission of pollutants such as heavy metals and polychlorinated dibenzodioxin and dibenzofuran (PCDD/PCDF).

Modern incineration plants are also known as *mass-burn incinerators* or *waste-to-energy plants* (Figure 1). With a typical consumption of 4500 m³ of air per ton of waste, most of the organic matter is oxidized and released into the atmosphere in the *flue gas* as H₂O and CO₂. After combustion three types of residual solid products are produced, whose nature and properties vary considerably with the composition of the waste and also with the combustion process itself: (i) *bottom ash*, which simply accumulates on the firing grate of the combustion chamber, is mainly composed of silicate glasses or minerals, and typically represents about 10 vol % 25–35 wt % of the original waste; (ii) *boiler ash* and *fly ash* (~3–6 wt %), which condense from the fumes during cooling as glass and other compounds such as salts; (iii) *air pollution control (APC) residues*

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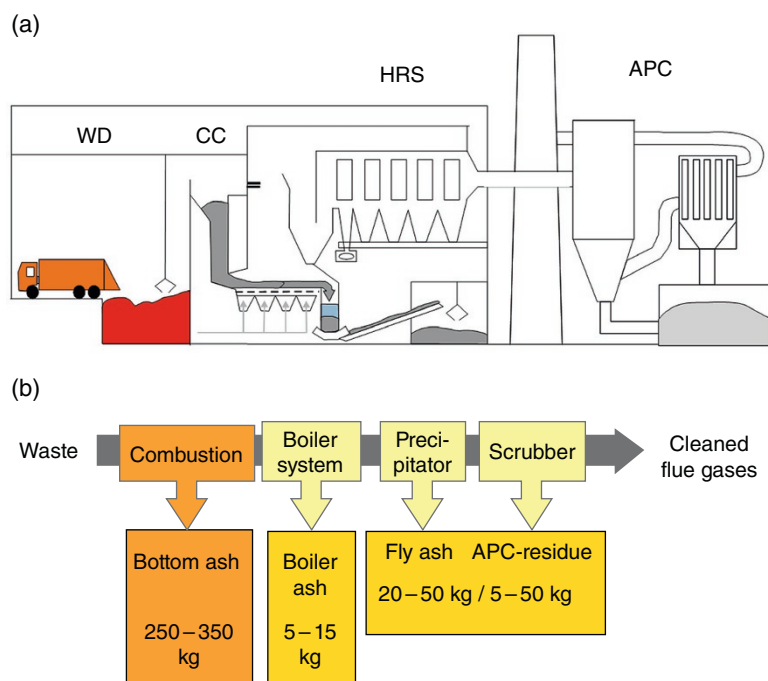


Figure 1 Sketch of an incineration plant from waste delivery to incineration (a) and recovery of the different types of residues (b). WD, waste delivery; CC, combustion chamber; HRS, heat recovery system; APC, air pollution control system.

(~1–5 wt %), mostly salts and dust (dry APC) or sludge (wet APC), which are eventually retrieved from the flue gas at the end of the process.

The reason why glass phases are major components of both bottom and fly ash is simply that Si and Al are themselves major elements of the initial waste. Particular attention will thus be paid to these glasses in this chapter, in relation to the other components of the residues with which they interact in various ways. And because environmental regulations keep becoming tighter, the long-term stability of these materials will also be dealt with in terms of complete vitrification and leachability of the residues. From sewage sludge to medical and electronic waste, a variety of other waste products will be finally considered because in each case vitrification is a possible solution for safe immobilization. The example of coal will illustrate the importance of the issue since the amounts of coal burned are very high. A single electric plant produces more than 125 000 tons of ash per year.

2 Municipal Solid Waste Incineration Residues

2.1 Conventional Combustion Plants (Grate Firing)

Municipal solid waste (MSW) is commonly called *trash* or *garbage* in the United States and *refuse* or *rubbish* in Britain. It is an extremely heterogeneous material whose

composition varies seasonally and differs from country to country owing to differences in lifestyles, waste treatment, and collection and recycling systems. In developed countries, it is mainly composed of kitchen waste, paper, plastics, metals, and other materials such as textiles, leather, rubber, e-waste, and various pigments often made of heavy metal oxides. It also includes inorganic materials not only as conspicuous glass, ceramics, concrete, or stone fragments but also as “hidden” components present at fractions of up to a few 10 wt %, for example, in plastics in which *fillers* (calcium and barium carbonates and sulfates, mica, or glass) are introduced to improve mechanical properties (Chapter 8.8) or to lower the amount used of the more expensive polymer and in paper and cardboard whose *coatings* (with kaolinite $[\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4]$, talc $[\text{Si}_4\text{Mg}_3\text{O}_{10}(\text{OH})_2]$, calcium carbonate, or titanium dioxide) ensure the smooth surfaces needed for high-quality coloring or printing.

Municipal waste has a calorific value for incineration ranging from 8 to 12 MJ/kg, a high quantity of kitchen waste lowering this value. Although combustion is stipulated to take place at least for 2 seconds at 850 °C, temperatures around 1000 °C are customarily favored to ensure complete burn off and to reduce the total organic carbon (TOC) content to less than 3 wt %. The manner in which metals partition upon combustion between bottom and fly ashes depends on their own physicochemical properties and on those of the compounds they form. Heavy metals with a low vapor pressure are retained in the bottom ash. Those elements with a high vapor

pressure and a low boiling point are expected instead to be transported with the flue gas so that they are enriched in the fly ash and/or APC residues. In consequence, Si, Al, Fe, and Cu mostly accumulate in the bottom ash, whereas Pb, Zn, Hg, Cd, and As have a higher tendency to be transported by fly ash. Overall heavy metals may represent up to 10% of the total mass of the ash.

2.2 Bottom Ash

Also called *grate ash*, *slag*, or *clinkers*, bottom ash is commonly wet discharged through periodic quenching in a water tank. These ashes are in general a mix of very fine, gray, porous material and larger chunks of glass, ceramics, metallic fractions, gravel, and rock (Figure 2). The main grain size of fresh bottom ash varies between sand (0.063–2 mm) and gravel (2–63 mm). Approximately 30–40 wt % of the bottom ash consists of fine-grained particles (<2 mm), 30–40 wt %, which vitrify and/or sinter upon combustion of the waste, 10–20 wt % represent incombustible matter (e.g. rock, ceramic, and glass), and about 10 wt % represent metals, usually Al, Fe, and Cu. A small part (<1 wt %) of the waste, including paper, plastics, and wood, may pass the combustion procedure unburned.

The dry density of bottom ash is higher than 1.5 g/cm³, whereas its specific density varies from 1.5 to 2.4 g/cm³. Depending on the waste input and combustion conditions, the composition of the fractions may also vary considerably (Table 1). Approximately 80–90 wt % of bottom ash consist of SiO₂, FeO, CaO, Al₂O₃, Na₂O, K₂O, and C in proportions similar to those found in basalts, whereas Mg, Ti, Cl, Mn, Ba, Zn, Cu, Pb, and Cr occur in the 1–10 g/kg range. Bottom ash also contains traces of Sn, Sb, V, Mo, As, Se, Sr, Ni, Co, Ce, Ag, Hg, B, Br, F, and I (Table 1). As for the water content (moisture), it varies from 15 to 25 % for wet quenching.

Regarding mineralogy, a variety of silicate and oxide compounds are found (Table 2) along with metals, which mostly remain in their native form, and hydrated phases forming in spite of the fast quench upon reaction with water. But the major phases are aluminosilicate glasses, representing 30–55 wt %. Parts of them represent residual fragments of the original waste (Figure 3). As expected from their source, these scrap glass particles are clear and transparent under the optical microscope, displaying light brown to yellow hues and dark or brownish striations [*schlieren*]. In contrast, the newly formed glass particles are commonly inhomogeneous and contain vesicles and crystalline inclusions. The color of the individual grains varies from transparent and dark to opaque (Figure 2b). Their light to dark brown sections mostly occur around partially melted metal fragments. They often contain various silicates

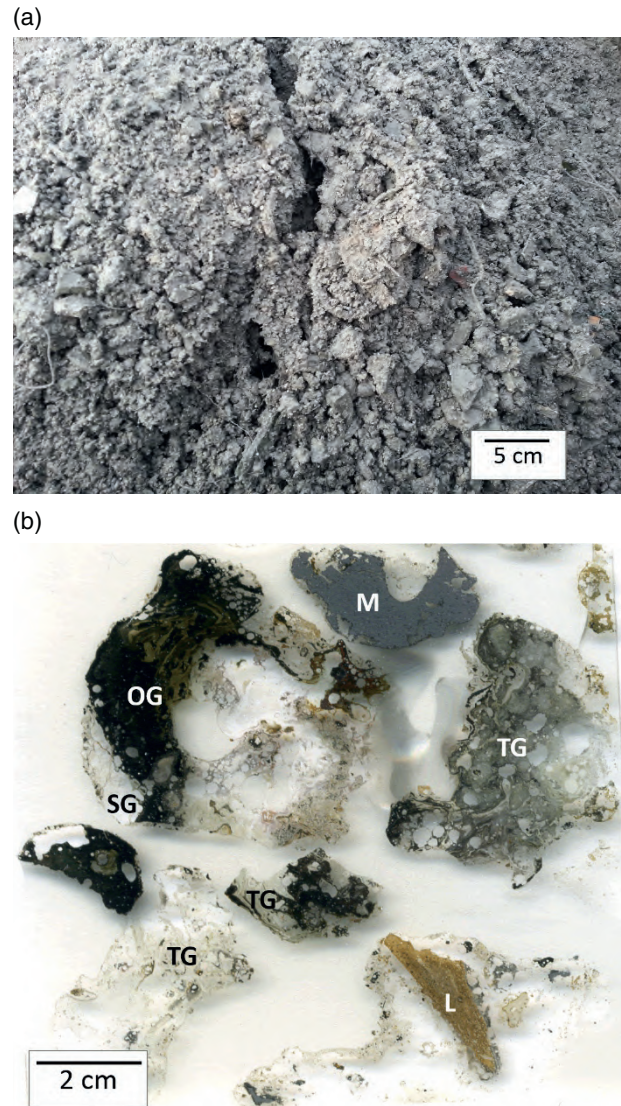


Figure 2 The heterogeneous nature of bottom ash. (a) As seen with the eye. (b) As seen at a low magnification in a thin section of porous MSWI particles: transparent (TG), opaque (OG), and scrap glass (SG) glass along with metal (M) and lithic (L) fragments.

and opaque phases with fewer vesicles than in transparent glasses. The terms *isotropic* and *opaque glassy* melt products are used for the transparent and dark particles, respectively [5].

The SiO₂ content of these vitrified particles is significantly lower than that of scrap glass (Table 3). The transparent glasses are characterized by higher concentrations of SiO₂ (55–70 wt %) and Na₂O (7–14 wt %) and low concentrations of FeO and Al₂O₃. In contrast, opaque glasses have high contents of CaO, FeO, and Al₂O₃ and low concentrations of SiO₂ (34–40 wt %) and Na₂O (3–5 wt %). Minor amounts of heavy metals are found only in opaque glasses.

Table 1 Overall chemical compositions of municipal waste incineration ash [2].

	Bottom ash (mg/kg)	Fly ash (mg/kg)	APC residue (dry/semidry)	APC residue (wet)
Ag	0.3–36.9	2–100	0.9–60	n.a.
Al	21.9–72.8 10 ³	49–90 10 ³	12–83 10 ³	21–39 10 ³
As	0.12–189	37–320	18–530	41–210
Au	<0.20	n.a.	n.a.	n.a.
B	38–510	n.a.	n.a.	n.a.
Ba	400–3 000	330–3 100	51–14 000	55–1 600
Br	1.4–150.2	n.a.	n.a.	n.a.
C	10–60 10 ³	n.a.	n.a.	n.a.
Ca	0.37–123 10 ³	74–130 10 ³	110–350 10 ³	87–200 10 ³
Cd	0.3–70.5	50–450	140–300	150–1 400
Cl	800–4 190	29–210 10 ³	62–380 10 ³	17–51 10 ³
Co	6–350	13–87	4–300	0.5–20
Cr	23–3 170	140–1 100	73–570	80–560
Cs	1–2	n.a.	n.a.	n.a.
Cu	190–8 240	600–3 200	16–1 700	440–2 400
F	200–1 100	n.a.	n.a.	n.a.
Fe	4.12–150 10 ³	12–44 10 ³	2.6–71 10 ³	20–97 10 ³
Ga	10	n.a.	n.a.	n.a.
Hg	0.02–7.8	0.7–30	0.1–51	2.2–2 300
I	2–10	n.a.	n.a.	n.a.
K	0.75–16	22–62 10 ³	5.9–40 10 ³	0.81–8.6 10 ³
La	2–20	n.a.	n.a.	n.a.
Mg	0.4–26 10 ³	11–19 10 ³	5.1–14 10 ³	19–170 10 ³
Mn	83–2 400	800–1 900	200–900	5–12 10 ³
Mo	2.5–276	15–150	9.3–29	1.8–44
N	110–900	n.a.	n.a.	n.a.
Na	2.87–42 10 ³	15–57 10 ³	7.6–29 10 ³	0.72–3.4 10 ³
Ni	7–4 280	60–260	19–710	20–310
O	40–500 10 ³	n.a.	n.a.	n.a.
P	1.4–6.4 10 ³	4.8–9.6 10 ³	1.7–4.6 10 ³	n.a.
Pb	0.098–13.7 10 ³	5.3–26 10 ³	2.5–10 10 ³	3.3–22 10 ³
Rb	40–50	n.a.	n.a.	n.a.
S	1–5 10 ³	11–45 10 ³	1.4–25 10 ³	2.7–6 10 ³
Sc	3–6	n.a.	n.a.	n.a.
Sb	10–432	260–1 100	300–1 100	80–200
Se	0.05–10	0.4–31	0.7–29	n.a.
Si	91–308 10 ³	95–210 10 ³	36–120 10 ³	78 10 ³
Sn	2–380	550–2 000	620–1 400	340–450
Sr	85–1 000	40–640	400–500	5–300
Ti	2.6–9.5 10 ³	6.8–14 10 ³	0.7–5.7 10 ³	1.4–4.3 10 ³
V	20–122	29–150	8–62	25–86
Y	10	n.a.	n.a.	n.a.
Zn	0.613–7.77 10 ³	9–70 10 ³	7–20 10 ³	8.1–53 10 ³
Zr	200	n.a.	n.a.	n.a.

Microscopic investigations show the growth of well-developed euhedral crystals or crystals with skeletal or hopper structures within the vitrified materials (Figures 4 and 5). These occur as isolated elongate laths or spherulites of acicular crystals [5, 7]. Isolated silicates

(melilite, pyroxene) or black octahedra or cubes of spinel phases can be observed within the dark schlieren (Figure 5). Isolated octahedra or cubic forms are typical of the oxide phases.

Table 2 Mineralogical and chemical composition of municipal waste incineration ashes.

Bottom ash [3]	Fly ash [4]
Amorphous phase (CaO–Al ₂ O ₃ –SiO ₂) ^a	Amorphous phase (CaO–Al ₂ O ₃ –SiO ₂)
Silicates (pyroxene, feldspar, melilite)	Chlorides (halite, sylvite, K ₂ ZnCl ₄)
Spinel (magnetite)	Carbonates (calcite)
Metallic fragments (Fe, Al, Si, etc.)	Sulfates (anhydrite)
Carbonates (calcite)	Phosphates (apatite, whitlockite)
Oxides (quartz, rutile)	Silicates (pyroxene, feldspar, melilite)
CaO and portlandite	

^a Na₂O (5.45 wt %), K₂O (0.50), CaO (9.79), MgO (0.01), MnO (0.01), FeO (0.50), TiO₂ (0.05), Cr₂O₃ (0.02), Al₂O₃ (27.83), SiO₂ (55.31), SO₃ (0.03).

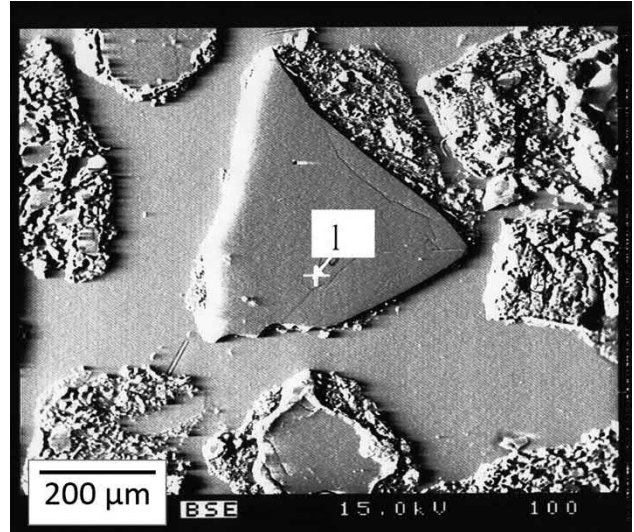


Figure 3 A scrap glass fragment of bottom ash shown in a backscattered scanning electron microscopy micrograph. The number refers to the analysis SP-1 of Table 2.

Table 3 Composition of scrap glass in MSWI bottom ash (SP-1 in Figure 3) and typical chemical composition of transparent (Tr, [5]) and opaque (Op, [6]) glasses and of glass particles obtained by advanced thermal treatment (K, [7]).

	SP-1	Tr-1	Tr-2	Tr-3	Tr-4	Tr-5	Op-1	Op-2	Op-3	Op-4	Op-5	K1	K2	K3
Na ₂ O	5.45	13.85	11.77	7.69	12.32	6.99	3.58	5.11	2.60	2.67	2.97	4.10	4.20	4.10
K ₂ O	0.50	1.13	1.64	1.60	1.19	1.06	0.44	1.37	0.35	0.21	0.21	3.10	3.50	1.90
CaO	9.79	9.47	9.87	8.90	4.05	12.56	26.63	12.84	22.15	26.16	27.69	26.00	19.60	29.80
MgO	0.01	2.33	0.47	0.86	1.07	2.61	3.78	2.03	2.44	3.77	3.21	4.40	2.80	4.50
MnO	0.01	0.00	0.00	0.01	0.07	0.07	0.10	0.43	0.21	0.17	0.23	0.27	0.17	–
FeO _{tot}	0.50	0.15	0.12	4.33	13.66	4.51	15.24	28.34	15.12	13.38	12.04	5.40	6.30	4.00
TiO ₂	0.05	0.06	0.02	0.31	1.01	2.16	0.94	0.83	3.93	3.37	2.67	1.10	1.40	–
Cr ₂ O ₃	0.02	0.02	0.00	0.03	0.02	0.03	0.09	0.00	0.10	0.38	0.06	0.15	0.22	0.30
Al ₂ O ₃	27.83	3.00	1.71	4.38	6.80	7.86	6.69	9.05	10.05	9.64	9.54	14.70	9.60	9.10
SiO ₂	55.31	68.28	69.03	61.19	55.74	57.60	39.55	37.72	34.79	34.75	35.51	35.40	44.50	43.30
P ₂ O ₅	–	0.17	0.19	0.24	0.66	0.55	0.61	0.77	0.96	0.61	0.67	2.50	2.50	2.40
ZnO	–	0.04	0.05	0.00	0.41	0.04	0.33	0.19	0.23	0.33	0.43	0.63	2.10	0.20
CuO	–	–	–	–	–	–	0.03	0.11	0.07	0.20	0.05	0.05	0.23	0.10
NiO	–	–	–	–	–	–	–	–	–	–	–	0.05	0.02	0.03
PbO	–	–	–	–	–	–	–	–	–	–	–	0.05	0.40	0.03
SO ₃	–	0.11	0.19	0.16	0.23	0.08	0.17	0.45	1.44	1.11	0.30	0.50	0.60	0.20
Cl	–	0.06	0.06	0.06	0.23	0.03	0.07	0.21	1.33	0.65	0.82	0.05	–	–
Total	99.50	98.67	95.12	89.76	97.46	96.15	98.25	99.45	95.77	97.40	96.40	98.45	98.14	99.96
NBO/T		0.57	0.52	0.40	0.33	0.46	0.70	0.34	0.54	0.68	0.74	0.89	0.66	0.97

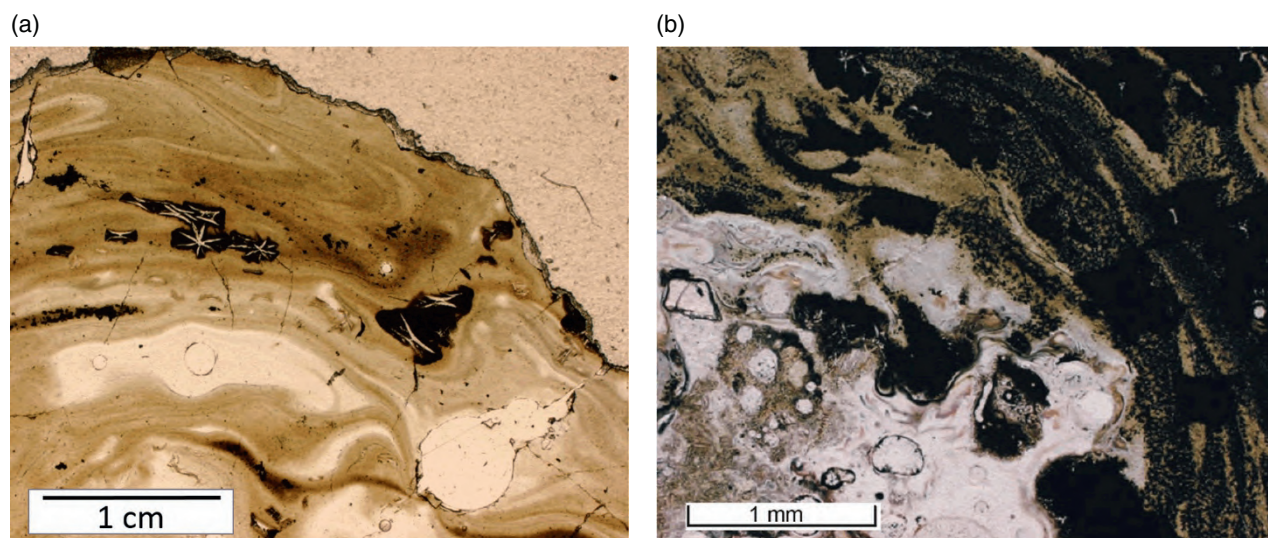


Figure 4 Transparent glass with yellow and brown *schlieren*. In the dark part, silicates (a) and oxides (b) crystallized preferentially.

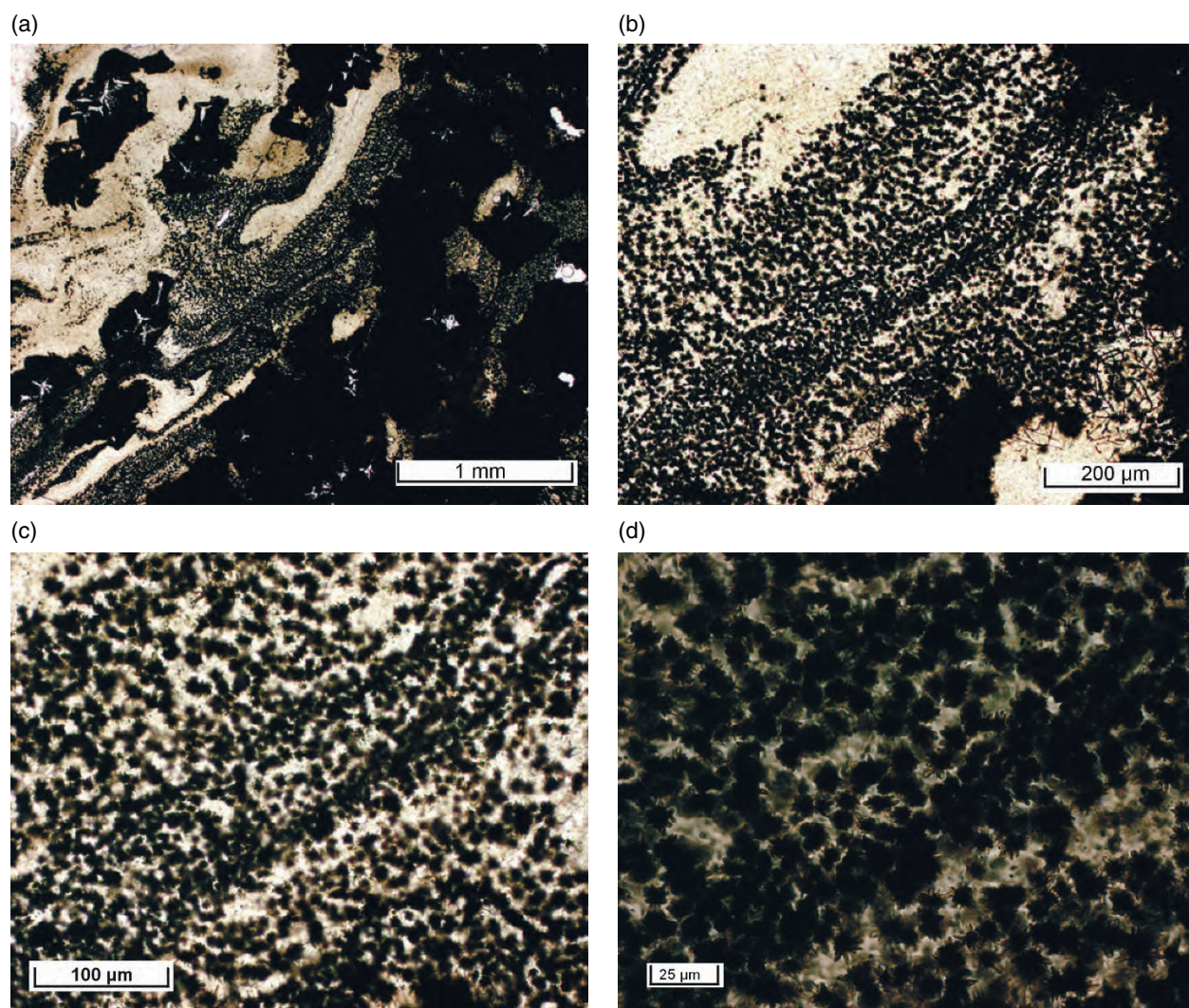


Figure 5 Crystallization of oxides and pyroxene along the dark *schlieren* in the glassy particles as seen at progressively lower scales.

2.3 Fly Ash and APC Residues

The flue gas transports dust particles and volatile compounds from the feedstock. These condense upon rapid cooling into particles smaller than 2 mm, called fly ash, whose specific density ranges from 1 to 4 g/cm³. Before any further treatment of the gaseous effluent, this loose material with an overall density lower than 1 g/cm³ is removed at the end of the heat transformation stage by processes such as electrostatic precipitation (Figure 1). Its nature and composition depend on various processes such as vaporization, melting, crystallization, and precipitation during incineration and subsequent treatment of the flue gas [4, 8]. A majority of these particles are chlorides and sulfates, which may deposit on the surface of the heat exchanger (hence their name *boiler ash*) and cause severe corrosion. Fly ash shows significant chemical and mineralogical heterogeneities even within individual particles. They are composed of volatile elements, notably K, Cl, Zn, and S, which are present as extremely fine-grained mixtures of chloride and sulfate minerals.

The rest of the particles represents up to 40 wt % of fly ash. They mainly consist of glass spheres 20–50 µm in

diameter with a relatively smooth surface (Figure 6), which are either hollow or filled, some of them bearing on their surface particles with a size of hundreds of nanometers. They are mainly composed of calcium aluminosilicates (Table 4, spots 6 and 7). In addition, crystalline oxides (quartz and metal oxides), silicates (melilite),

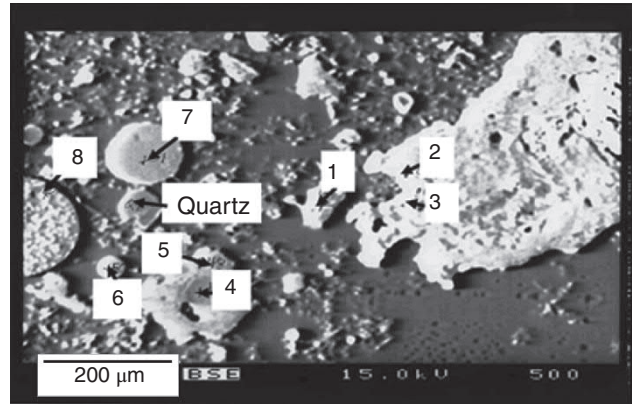


Figure 6 The heterogeneity of fly ash as seen in a backscattering electron image of glassy spherulites. The numbers illustrate the location of EMPA spot analysis and refer to analyses in Table 4.

Table 4 Chemical composition of fly-ash particles (wt %, electron microprobe analyses EMPA).

Chemical composition (wt %)	Spot 1 Garnet	Spot 2 Ca–Ba–Fe–Si–O	Spot 3 Ca–Fe–Si–O	Spot 4 Ca–Al–SO ₄ –Cl–O	Spot 5 Ca–Al–SO ₄ –Cl–O	Spot 6 Glass	Spot 7 Glass	Spot 8 Quartz
Na ₂ O	1.21	1.06	0.02	1.65	0.24	4.64	0.64	0.19
MgO	1.72	1.34	5.96	0.19	0.54	4.90	2.71	0.01
Al ₂ O ₃	9.60	4.29	2.27	72.54	30.41	15.20	8.07	0.13
SiO ₂	21.80	26.18	2.44	0.13	0.64	36.83	27.21	94.59
P ₂ O ₃	7.81	1.66	0.15	0.07	0.05	3.33	2.53	0.03
SO ₃	0.31	0.10	0.16	8.03	13.55	0.06	4.08	0.10
Cl°	0.08	0.06	0.01	1.54	5.86	0.04	0.08	0.12
K ₂ O	0.60	0.20	0.05	1.88	1.74	0.91	0.20	0.16
CaO	25.17	20.49	2.35	7.16	19.32	18.78	45.71	0.31
TiO ₂	2.65	8.30	2.16	0.00	0.00	1.71	0.34	0.07
Cr ₂ O ₃	0.08	0.03	0.49	0.00	0.05	0.02	0.09	0.00
FeO	20.39	10.93	63.98	0.16	0.14	9.27	4.11	0.64
NiO	0.18	0.05	0.66	0.00	0.08	0.06	0.01	0.03
CuO	0.15	1.54	4.39	0.43	1.10	0.21	0.25	0.08
ZnO	0.14	0.65	3.60	4.08	3.25	0.67	1.20	0.41
CdO	0.08	0.00	0.07	0.00	0.11	0.06	0.00	0.07
SnO	0.02	0.04	0.13	0.00	0.01	0.07	0.07	0.02
BaO	1.45	18.26	2.01	1.09	4.00	0.33	0.00	0.00
PbO	0.00	0.40	0.00	0.00	1.34	0.14	0.00	1.39

alloys, and metal (Si) compounds are present. As for heavy metals, they can occur as oxides like Pb_3O_4 and PbO but are in most cases bound in the glass (spots 2–5 in Table 4) and magnetic phases.

After fly-ash condensation, the flue gas still carries many impurities that must be removed to meet the emissions limits for specific pollutants before being released into the atmosphere. The composition of the resulting APC residues then depends on the cleaning procedure adopted, e.g. dry adsorption, quasi-dry process, or wet scrubbing. The amount of APC residues usually ranges from 2 to 5 wt % of the original waste [8]. The amount of heavy metals in the salt-rich fraction is high. Because of contamination with dioxin and furan, this fraction is classified as hazardous waste. This ash is highly soluble as about 25–85 wt % of the material can dissolve in water. According to their distribution coefficients, the highly volatile species accumulate in the fly ash and/or APC residues, leading to the higher concentration of Pb, Zn, Hg, Cd, and As in fly ash.

2.4 Dry Discharge of Bottom Ash

A new dry-discharge technology has been recently introduced. An additional (tertiary) air inlet is installed at the end of the combustion chamber. On one side, it cools down the bottom ash. On the other, it supports the after-burning of organic particles during the incineration process and leads to a reduction of the TOC content by more than 50%. As a result, the loss of ignition (LOI) is insignificant for dry compared with wet-discharged ash, and the separation of the particles is much easier because agglomeration of the finest particles is avoided. It follows that the recovery of metals, both ferrous and nonferrous, and also mineral particles is more efficient. Further benefit of this procedure is a drastic decrease of the leachability of heavy metals. During the procedure, very fine particles are generated, so this dust emission needs special treatment. One concept is to separate the dust in situ and recirculate it to the combustion chamber together with the tertiary air inlet.

2.5 Advanced Thermal Treatment by Pyrolysis and Gasification

In Western countries, waste is mostly burned between 800 and 1000 °C. Few attempts have been made at vitrifying the residues. In Eastern countries (e.g. Japan, Taiwan, or China), in contrast, vitrification of MSW and of fly ash sewage ashes is more usual. Particularly in Japan, a long debate in the 1990s about dioxins in residues initiated a new incineration technology aiming for

decomposing dioxin components and reusing the molten residues. In this case the content of vitrified material can range between 60 and 85 % of the total volume of the particles.

In one concept, solid waste is melted between 1300 and 1700 °C by a plasma arc, an electric resistance, a coke bed, or a fluidized bed heated by waste combustion. Another concept is waste pyrolysis, which is based on the thermal degradation of a substance in the absence of oxygen at rather low temperatures of 300–850 °C. The result is a mixture of gases termed *syngas* with a high calorific value ranging from 10 to 20 MJ/m³ (referred to room pressure and temperature). In general, metals and inert materials (such as rubble) are separated before the glass waste is processed.

Yet another concept is a two-step gasification system [9, 10]. Metals, glass, and other materials that cannot be gasified are separated from the waste stream before the onset of the gasification process. The first step is a combination of pyrolysis and combustion with partial oxidation of the waste above 650 °C. It includes the conversion of waste into a secondary energy carrier. In the second step, the residues are vitrified above 1300 °C to ensure a decrease of the PCDD/PCDF concentrations. Here, an option is to separate the heavy metals with the lowest boiling points during the first step and recover them as metals.

In contrast, the highly volatile compounds accumulate in the fly ash, where more than 90 % of Cl, 95 % of Pb, and 92 % of Zn are found.

Vitrification of waste by the Siemens Thermal Waste Recycling Technology [7] is a concept comparable with a gasification–vitrification procedure. The waste is first pre-degraded thermally at 450 °C. After removal of metals and inert particles, the remaining material, mainly consisting of C, SiO_2 , CaO, MgO, and Fe_2O_3 , is burned at 1300 °C. About 95–99 % of the particles formed are glassy, whereas only 1–5 % consist of crystalline phases like melilite, pyroxene, and spinel. These glass particles are more homogeneous than observed for the vitrified compounds obtained by conventional combustion. As indicated by the results of three different campaigns (Table 4), remarkably low contents of SiO_2 and high concentrations Al_2O_3 are observed, which are similar to those of opaque glasses [7]. The amounts of P_2O_5 , SO_3 , and heavy metals in these glasses are high. In general these metals are incorporated in the spinel phase. A detailed study of the relationships between the chemistry of bottom ash and the observed mineral phases has shown that high alkali and low silica concentrations favor the formation of melilite, whereas lower alkali contents and high silica contents promote the crystallization of plagioclase feldspars and/or pyroxenes [5, 7].

3 Environmental Impact of MSWI Residues

3.1 Leachability

Weathering is a spontaneous process whereby a material reacts to adapt to changes in parameters of its environment such as pH, redox potential, temperature, and humidity conditions as well as to the concentration of reacting agents (e.g. CO_2). Several interrelated processes may occur, including hydrolysis, pozzolanic solidification, dissolution/precipitation, carbonation, oxidation/reduction, surface complexation, sorption, ion exchange, and formation of solid solutions as well as mineral neoformation [8]. The alteration of MSWI residue leads to the mobilization of various species. The stability of crystalline and glass phases determines the leachability of heavy metals in bottom and fly ashes. Continuous mineralogical changes over time and the formation of new phases control the leachability of the residues. Therefore, the release of soluble species, namely, heavy metals and salts, may vary significantly with time.

Alteration of MSWI residues causes significant change in mineralogy. Newly formed minerals are anhydrite and gypsum [$\text{CaSO}_4(\text{H}_2\text{O})_2$], ettringite, hydrocalumite [$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$], (Fe-containing) Ca-(silicate) hydrates (e.g. C-S-H, C-A-H), gibbsite [$\text{Al}(\text{OH})_3$], rosenhahnite [$\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_{1.9}(\text{CO}_3)_{0.1}$], zeolite, hematite, ferrous iron oxide, kaolinite, calcite, and amorphous phases [11–13]. As already stated, toxic ingredients are typically present as salts in fly ash. Chlorides such as halite [NaCl] and sylvite [KCl] are commonly identified. They control the leaching of Cl, K, and Na, whereas leaching of Zn may be due to the dissolution of K_2ZnCl_4 and ZnCl_2 . Heavy metal salts and hydroxides are often observed, e.g. CuCl_2 , $2\text{CuCl}_2\cdot\text{H}_2\text{O}$, ZnSO_4 , amorphous ZnO , calcium hydroxozincate [$\text{Ca}[\text{Zn}(\text{OH})_3]_2\cdot 2\text{H}_2\text{O}$], malachite [$\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$], azurite [$2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$], yellow-brown lepidocrocite [$\gamma\text{-FeOOH}$], and goethite [$\alpha\text{-FeOOH}$] or FeCl_2 , FeCl_3 [11, 13].

3.2 Alteration of Glass Particles

Because studies of MSWI bottom ash have focused on long-term leaching, only a few of them have described the alteration of the glass phases. With aging, it appears that the glass fraction decreases from a maximum of 45 wt % to around 30 wt % [12]. Leaching first causes the formation of a gel layer because of the reactivity of the vitrified particles. Depending on glass composition, different reactions may occur in an open environment with high rates of water infiltration: (i) in situ transformation on the surface of the silica-rich glass and (ii) formation

of a leaching layer by preferential dissolution of the network modifiers of aluminosilicate glasses and formation of an amorphous or partly crystalline phase on the surface [14]. After one week of leaching, the first effects observed at the glass surface are precipitation of calcium silicate hydrates such as ettringite, tobermorite [$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2\cdot 4\text{H}_2\text{O}$], zeolites (likely Ca chabazite [$(\text{Ca},\text{K}_2,\text{Na}_2)_2[\text{Al}_2\text{Si}_4\text{O}_{12}]_2\cdot 12\text{H}_2\text{O}$]), natrolite [$\text{Na}_2(\text{Al}_2\text{Si}_3\text{O}_{10})\cdot 2\text{H}_2\text{O}$]), and hydroxyapatite [$\text{Ca}_5(\text{OH})(\text{PO}_4)_3$] [11]. This assemblage results from a pH higher than 10 and high concentrations of chloride and sulfate in the solution. The kinetics of course largely depends on the environmental and boundary conditions. At acid or alkaline pH, the alteration of glass is much faster than at intermediate values. In a study of long-term natural weathering of glasses in MSWI bottom ash, the formation of a well-ordered illite clay was observed after 12 years [14]. In general, the weathering of glass phases in bottom ash is faster than that of natural glass [14, 15].

The transformation of glass is sensitive to environmental factors such as temperature and moisture. Changes in these parameters may cause shrinkage or expansion of the gels [15], whereas alkalinity regulates the Si/Al ratio of the solution and, thus, the Si/Al ratio of the amorphous hydrous aluminosilicate phase as an intermediate reaction product [14]. Besides, the mechanical liberation and/or dissolution of the embedded metal inclusions has an impact on the alteration of the glass whose dissolution may lead to the dispersion of the heavy metals within an unknown time frame [13].

The long-term alteration of glass obtained by an advanced thermal treatment termed *Schwel-Brenn-Verfahren* has been studied for a glass first homogenized at 1500°C and then tempered at $700\text{--}750^\circ\text{C}$ [7]. Dynamic leaching performed with distilled H_2O at 100°C in a Soxhlet extractor retarded the development of saturation effects on the surface of the glasses. After a reaction time of 1000 hours, the surface was completely covered by a brownish layer depleted in Si and Al and enriched in Fe, Cr, Cu, Mn, and Zn. The formation of goethite and hydroxyapatite was attributed to congruent dissolution of the glass. The corrosion rate of this glass is high, being four times faster than for volcanic glasses under the same conditions.

In a second dynamic test, an accelerated leaching procedure was performed at 200°C and pH 12.5 [7]. After a 100-day reaction under $\text{Ca}(\text{OH})_2$ saturation conditions, the solution was cooled down to ambient temperature, and the precipitates were analyzed. The growth of tobermorite $11\text{ \AA}$ and natrolite on the glass surface was observed. The presence of these minerals matches with the results of weathering studies of bottom ash [11, 14]. Glass leaching at room temperature and pH 11 caused an

increase in Zn and Cu concentrations in the solution up to 20 mg/L. This result indicates an enhanced release of heavy metals with time. The occurrence of etch pits on the surface was accompanied by a depletion of alkali and earth alkali elements. Furthermore, quartz and clay minerals of the montmorillonite group covered the surface.

The stability of the vitrified particles is a key factor in the long-term evolution of bottom ash. It can be roughly estimated from the calculated bulk polymerization of the glass as given by the ratio of nonbridging oxygens to tetrahedral cations (Chapter 2.4). Whereas this NOB/T ratio varies from 0.3 to 0.7 for opaque glasses, it is about 0.5 for transparent glasses (Table 4). Such rather low values translate into relatively ready corrosion. Vitrification of the residues at higher temperatures thus ensures a better glass stability as it causes the NOB/T ratio to increase to values in the range of 0.66–0.97 (Table 4).

3.3 MSWI Ashes as Aggregate Materials

Because untreated MSW residues are waste materials usually disposed of in landfill sites, efforts have been made to transform them instead into useful materials. Limitations in this respect result from the leachability of toxic heavy metals such as Pb, Cd, As, Sb, Hg, Sn, Cr, Zn, and Cu and from the high amounts of chlorides and sulfates concentrating in bottom and fly ashes and in APC residues. This is why both residues are classified as hazardous waste and require special control. Hence, the issue at stake here is the immobilization of toxic components and, in addition, the destruction of dioxins in fly ash.

Washing of MSW residues reduces the concentration of these elements, in particular of chlorine, to acceptable levels [8, 10]. The extraction of heavy metals depends on pH and liquid to solid (L/S) ratio as well as on the extracting agent [8]. Bottom ash treated in this way can be utilized as road base material, in cement and concrete production, as interim landfill cover, or as backfill material. Fly ash is often applied in cement and concrete production. In some cases, the harmful elements in the MSW residues are immobilized in the matrix [8], e.g. by solidification with cement, or stabilized with substances such as phosphates, ferrous sulfates, colloidal aluminate oxide, sodium sulfide, or calcium aluminate.

In view of the long-term reactivity of fly ash, vitrification has been considered as an interesting alternative to immobilize their toxic components. Numerous studies have aimed at producing a glass or glass ceramics either directly from the solid waste or by addition of various components. The main option is to obtain durable materials with a minimum of glass-forming or glass-modifying additives. These materials should consist of a glassy matrix with 50 up to 95 vol % crystalline materials. An

overview of the different studies has been given [10], whose main features are summarized below.

A comparison of conventional and advanced thermal treatment systems confirms that the fraction of vitrified particles increases with the combustion temperature and combustion time, so it is possible to vitrify bottom ash without additives above 1400 °C. At higher temperatures a metallic melt mainly composed of a Fe–Cu alloy and P, C, S, Si, Ni, Cr, W, Sn, Sb, and Na impurities can be separated from a silicate melt with small quantities of S, P, Cu, Zn, Ba, Pb, Cr, and Mn [10].

Vitrification of fly ash at 1350 °C causes increases in the contents of SiO₂ (19.8 → 43.2 wt %), MgO (3.8 → 7.5), and Al₂O₃ (7.0 → 15.5) and significant decreases in those of Na₂O (6.7 → 0.2) and K₂O (6.2 → 0.7) as a result of alkali volatilization [16]. This procedure generates secondary ash, however, which comprises 10 and 60 wt % of heavy metal and alkali chlorides, respectively [10]. This secondary ash is returned to the vitrification furnace. Less than 1 wt % chlorine then remains in the glass so the leachability of toxic species is markedly reduced. Washing the fly ash to remove chlorine and imposing a high partial pressure of oxygen promote the retention of heavy metals in the solids during vitrification [10].

Hydrothermal treatments of fly ash modify the mineralogical compositions and, thus, the relative proportion of aluminosilicate glasses and crystalline phases like tobermorite, a hydrogarnet mineral close to katoite, and zeolitic compounds. These glasses are the most abundant and most unstable phases during the hydrothermal treatment [17].

To optimize the relative ratios of Al₂O₃, SiO₂, and Na₂O for melting bottom and fly ash, additives have also been tested in the form of glass cullet, feldspar, or clay by-products. In general, additives improve the mechanical properties of the mineral phases crystallizing from the melt, which are diopside [CaMgSi₂O₆], wollastonite, and anorthite [CaAl₂Si₂O₈]. The optimal results for chemical durability have been obtained with the addition to bottom ash of 4 wt % fly ash and 43 wt % feldspar. Because it has also been recognized that chlorides have a negative effect on vitrification, either fly ash should be washed to remove the soluble salts or MgO or SiO₂ be added for melting at the higher temperature of 1500 °C.

Many studies have dealt with the production of glass ceramics from vitrified ash. In these cases the duration and temperature of the heat treatments are of course the fundamental parameters. The sintering process is affected by addition of clay or alumina waste [10]. Building materials with pink, black, reddish brown, and blue colors have even been produced from bottom-ash-based glass ceramics with various additives like TiO₂, MnO₂, Fe₂O₃, or glaze of cobalt aluminum oxide [18].

As expected, tests indicate that these glass ceramics possess better mechanical and thermal properties than their parent glasses (Chapter 7.11). Applications for ash vitrified at temperatures above 750 °C include road base material, blasting grit, embankments, and production of construction and decorative materials like ceramic tiles, pavement bricks, and water-permeable blocks [19]. A special case involves the *thermite* pyrotechnic process whereby melting is achieved by a strongly exothermic redox reaction caused by the reduction of a metallic or a nonmetallic oxide (e.g. FeO) by a metal (e.g. Al). Mixtures containing up to 30 wt % fly ash have been successfully melted in this way at temperatures from 1350 to 2200 °C [16] to yield more than 91 wt % of iron as an alloy and the other nonreactive oxides as slag. The latter incorporates the heavy metals in the glassy matrix. With increasing temperatures, Cd increasingly partitions into the flue gas, whereas Pb, Zn, and Cu preferentially remain in the vitrified particles.

4 Special Residues

4.1 Residues of Coal (Co-)combustion

About 40% of the world's electricity needs are provided by combustion of coal at temperatures higher than 1200 °C in power plants. The calorific value of the coal determines the ash content, which is typically about 10 wt % but can be as high as 40 % for the lowest grades [20]. As one of the largest types of industrial waste, these coal combustion residues (CCR) also include fly ash (60 %), bottom ash (15 %), and boiler ash (<2 %) along with flue-gas desulfurization (FGD) materials (25 %), which may be used to produce gypsum. About 780 million tons of CCR have been produced worldwide in 2010 and 130 in 2014 in the United States alone.

In general, fly-ash particles have a spherical shape whose size ranges between 0.5 and 300 µm. They mainly consist of amorphous, quenched glass composed of SiO₂, Al₂O₃, Fe₂O₃, and minor amounts of CaO. The mineralogy includes quartz (or partly cristobalite), mullite [SiO₂·2Al₂O₃], and the iron oxides hematite, magnetite, and/or maghemite [γ -Fe₂O₃]. Anhydrite, free lime, portlandite, calcite, periclase [MgO], sylvite, halite, rutile, and anatase [TiO₂] may also occur. In Ca-rich fly ash, the main phases identified are anorthite, gehlenite [CaAl₂Si₂O₇], and åkermanite [Ca₂MgSi₂O₇] (the main end members of the melilite group) and various calcium silicates and calcium aluminates.

Depending upon the specific coal-bed properties, CCR may include one or more of the following partly hazardous species, mostly in trace concentrations: B, Cd, Cr (as Cr⁺⁶), Co, Pb, Hg, Mn, Mo, Se, Sr, Th, and V, light

metals (Be), or metalloids (As, Sb). Coal in addition contains naturally occurring radioactive materials (NORM), including U, Th, Ra, and Rn. These elements are preferentially concentrated by a factor of 10 or more in the fly ash where their concentration can, for instance, reach about 150–180 ppm for uranium. Although the radioactivity released can then be higher than around a nuclear power plant, the levels remain well below the safety limits.

Upon combustion very small concentrations of organics like dioxins and polycyclic aromatic hydrocarbon (PAH) compounds could be available. It is these organic compounds that make the utilization of fly ash problematic. Depending on coal composition, two types of fly ash classes are defined by ASTM C618 (American Section of the International Association for Testing Materials): (i) obtained from anthracite and bituminous coal, class F ashes possess pozzolanic properties but need a cementing agent as a result of their lime content lower than 7%; and (ii) as residues of lignite or subbituminous coal combustion, class C ashes contain more than 20% CaO and higher amounts of alkali and sulfates.

Usually these residues are landfilled either directly or after binding with concrete. In the United States, about half of them are recycled as a partial substitute for Portland cement in concrete production. These pozzolanic qualities are in addition put to use to encapsulate these residues in wallboard, roofing materials, and bricks. Attempts have also been made at using them in road base construction, soil amendment, land reclamation, and zeolite synthesis, as filler in polymers, and even as fertilizers in agriculture [10].

Vitrification of CCR has also been investigated, for instance, for obtaining a starting material replacing kaolinite in the production of cordierite ceramics. For vitrification of coal fly ash, temperatures higher than 1400 °C are necessary. Addition of MgO and TiO₂ decreases the viscosity of the melt. A DSC analysis showed that the nucleation rate reaches its maximum at 620 °C with Li₂O [10]. Depending on the ash composition, however, additives are indeed needed to obtain stable glasses (with more SiO₂) or glass ceramics (with less SiO₂). In one study, two different types of glasses were, for instance, obtained when ashes were mixed with glass cullet or dolomite and vitrified at a maximum temperature of 1500 °C. Glass conversion began at 600 °C for Na₂O–CaO–Al₂O₃–SiO₂ and at 670 °C for CaO–MgO–Fe₂O₃–Al₂O₃–SiO₂. Crystallization of pyroxene and wolastonite, and hence formation of glass ceramics, was achieved in the 900–1100 °C range. Either dense materials without open porosity or solid foams were obtained. One can also form samples by cold pressing followed by sintering in the 1125–1200 °C range. The materials exhibit high durability and low leachability. Likewise, glasses with an excellent durability can be obtained from fly ash.

4.2 Sewage and Dredging Sludges

Sewage sludges have high water contents of 50–70 %, so they are usually dewatered and/or partially dried. On a dry basis, their carbon content is about 30 wt %, and they bear a similar fraction of inorganic matter, which mainly consists of SiO_2 , Al_2O_3 , CaO , and P_2O_5 , together with small amounts of Fe_2O_3 , MgO , K_2O , and sulfate and trace amounts of the heavy metals Pb, Cd, Ba, Cu, Cr, Zn, and V [10]. This sludge is often landfilled or even dumped in the sea. Thanks to its high phosphorus content, it has alternatively been utilized as fertilizer on farmland. The occurrence of pathogens, micropollutants including sterols and hormones, and potentially toxic elements like Cd, Cu, Pb, Hg, Mo, Ni, Se, and Zn have raised in many countries concerns over agricultural uses of this waste. Incineration offers an alternative [10]. Combustion can be performed in fluidized-bed furnaces between 850 and 900 °C, but the fly ashes produced have then to be disposed of. Attempts have also been made at producing glasses and glass ceramics (see [10] for a review) with, for example, addition of fly ash, limestone, galvanic waste, or fluorite for vitrification between 1200 and 1450 °C. After sintering of the glass powder at 725 °C, glass ceramics with diopside and/or anorthite, depending on the bulk composition of the glass, have been alternatively obtained.

Dredging sludge removed from harbor basins or waterways may also contain relatively high concentrations of heavy metals (Mn, Pb, Cd, Zn, Hg), of metalloids (As, Se), and of other pollutants (organic hydrocarbons, PAH). These sludges are often dumped in the sea or are landfilled. In this case, one favors either bioremediation by introducing microorganisms to break down contaminants or stabilization by adding cement or bentonite clay to make handling easier. Because Cd, Cu, and Cr are often adsorbed by oxidizable organic matter and sulfides, exposition of the sludge to air causes oxidation of the reduced species, whereas acidification of the sludge by bacterial activity promotes the mobilization of the toxic elements. In view of their own low calorific value, dredged sediments must be mixed with high-caloric materials to make incineration possible, whereas addition of other materials is needed to adjust their high SiO_2 , Al_2O_3 , and CaO contents and low Fe_2O_3 , MgO , Na_2O , and K_2O concentrations. As an example [10], glass may be produced after mixing with MSWI ash and melting from 1300 to 1500 °C. By addition of glass cullet, the temperature needed decreases to 1200–1350 °C. In another study pellets of glass powder sintered at 937 °C have yielded glass ceramics with pyroxenes (diopside, augite) and melilite (gehlenite, akermanite) as major crystalline phases.

4.3 Special and Hazardous Waste

For incineration of hazardous waste, legal regulations restrict the emissions of organics, hydrogen chloride [HCl], and particulate matter (PM), as well as those of volatile components. To convert ash and metal residues into a stable glass form, one typically uses controlled-air incinerators, liquid injectors, fluidized-bed incinerators, or rotary kilns. These technologies are expected to achieve complete combustion above 1100 °C with sufficient combustion times. The composition of the ash depends on the primary characteristics of the waste. They are typically composed of carbon, salts, and metals.

Waste from the zinc hydrometallurgical process and red-mud waste have in general high concentrations of Fe_2O_3 , ZnO , PbO , SiO_2 , and CaO with smaller amount of Cu, As, Ni, Na, K, Al, Ti, and S [10]. To be vitrified, they can be mixed either with primary materials like sand, feldspar, limestone, or dolomite or with other waste like glass cullet, electric-arc furnace dust, carbon, or fly ash and then heated at 1400–1450 °C or even at lower temperatures after pretreatment at 850 °C. The products obtained are glass–ceramic paving tiles, covering panels, or glass fibers for insulation [10]. A particular type of hazardous waste is red mud from processing and extraction (without additives) of beryllium metal from beryl ore containing 1 to 1.7 wt % BeO . The leachability of Be in the vitreous opaque products decreases when samples are prepared at high temperatures (650 µg/g at 850 °C and only 0.04 µg/g at 1600 °C) [10].

Blast-furnace slags and dust from electric-arc furnace may also contain significant concentrations of Zn, Pb, Cu, Cr, Ni, Cd, and Mn, in addition to As or Ba, and be enriched in phosphorus. With the processes developed in the 1960s by British Iron and Steel Research Association, and independently in former Soviet Union, both yield without additives glass ceramics (*slagceram* and *slagsital*) containing (pseudo)wollastonite and anorthite or diopside, which have been commercialized in the construction industry thanks to their excellent mechanical properties, chemical durability, and high resistance to abrasion. In addition, glass and glass ceramics with sometimes very good durability have been prepared from mixtures with quartz sand or powder, feldspar, or kaolinite, Ca and NaH carbonate, glass cullet, or borax [10].

Cement dust has also been declared hazardous because of its very fine grain size. Likewise, plaster-contaminated building materials are considered as problematic because of the sulfate leachability from gypsum. Vitrification of these dust mixtures together with 30 wt % sodium borate glass has been achieved at 1100–1200 °C [10].

In metal-finishing and plating industries, heavy metals like Cu, Cr, Ni, Zn, and Pb occur in the galvanic waste with average contents of 10 wt % but also higher values

up to 40 wt %. Depending on production line and treatment procedure, this waste also contains high concentrations of calcium hydroxide, sulfate, chloride, or phosphate but practically no silica. To make vitrification possible, more than 60 wt % of silica-rich materials have to be added, for instance, in the form of feldspars or waste material from various industrial branches [10]. In most cases, colored glasses or glass ceramics are obtained. Additionally the production of alkali-resistant glass fibers has been proposed [10].

In the leather industry the hazard is caused by high Cr concentrations. Upon incineration Cr^{6+} -rich ashes are obtained, which could be used to produce colored porcelain tiles. Remarkable is the utilization of waste with up to 30 % Cr for vitreous ceramic bodies. When mixed with soda-lime glass, TiO_2 , and MgO , and pressed in bars, they vitrify at temperatures lower than 1000 °C. The leachability of chromium decreases with increasing annealing temperature [10].

Wastes with asbestos are classified as particularly dangerous not at all because of heavy metals or other pollutants, but because of the effects on human lungs of fibrous minerals such as amosite $[(\text{Fe,Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2]$ and crocidolite $[\text{Na}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH,F,Cl})_2]$. Although various concepts have been proposed to treat them chemically before disposal, the most common practice is to seal them in big bags for storage in controlled landfill sites, sometimes after immobilization in cement to prevent the fibers from being exposed. Attempts have nonetheless been made at decomposing asbestos by calcination and annealing at high temperature to get secondary ceramic raw material. These include thermochemical pyrolysis (conversion in absence of oxygen) or plasma-arc treatment. Microwave heating has also been used successfully to vitrify asbestos. Temperatures of 700 °C are necessary to convert cement-asbestos materials to destroy the asbestos minerals. A retreatment with sodium hydroxide makes it easier to handle it. A special procedure is GeoMelt®, which relies on Joule melting and is also used to treat radioactive waste. It is an in situ vitrification technique and similar to the melting procedure used to treat contaminated land [10].

Electronic waste (e-waste) or *waste electrical and electronic equipment* (WEEE) is becoming an increasingly important issue as a secondary resource material for heavy metals and rare earth elements. Along with refrigerators and other appliances, it includes computers, monitors, printers, scanners, data storage devices, servers, networking systems, copiers, fax machines, radios, TVs, cell phones and pagers, entertainment device electronics, etc. Pyrometallurgy and hydrometallurgy are used to recover valuable metals. As exemplified by cathode-ray tubes (CRT), e-waste contains special glasses with high

concentrations of Pb, Ba, or Sr [10]. Various types of glass–ceramic composites have been produced by sintering at 930 °C of CRT glass cullet mixed with other materials such as dolomite and single-crystal alumina platelets. Alternatively, CRT cullet has been either used as a flux to produce tiles or mixed as sludge with calcium fluoride and melted at 1200 °C to obtain glass ceramics. Disposal of different kinds of batteries (Zn–carbon, Ni–Cd, Ni–MH, Li, Ag) has also to be considered. After extraction of the heavy metals from the metallic fraction, slags have been produced by vitrification of alkaline batteries with dolomite, lime, and glass cullet at 1450 °C in graphite crucibles.

As for medical waste, this material is very inhomogeneous. It includes infectious and noninfectious material and possibly radioactive elements. It is partly treated by chemical disinfection or sterilization and afterward disposed in landfill sites, but most of it is incinerated, generally at temperatures higher than 1100 °C. The residues are comparable with MSWI bottom and fly ashes. Another method is plasma-torch melting, which is used to melt the waste at 1550 °C and yield a vitreous slag and a metallic fraction [10].

5 Perspectives

With socioeconomic development the volume of waste has increased tremendously over time, which has sustained a parallel growth of landfills all over the world. Leaving aside the much more important industrial or construction waste, 300–400 kg of domestic waste is, for instance, produced per person and per year in Europe. If 36 % of the waste is recycled, the rest is landfilled or burned. The introduction of incineration in the late nineteenth century has thus represented a convenient way to reduce drastically the volume of waste and, in addition, to immobilize contaminants and to eliminate many toxic agents and substances. These advantages have made incineration of municipal waste a standard method in most industrial countries, in particular when land space for disposal is scarce, which has proven to be a safe method to treat hazardous and clinical waste. Although air pollution caused by the emissions of heavy metals or organic pollutants is now technically and legally controlled, the occurrence of leachable toxic compounds in combustion residues and of tiny glass particles and other reactive components makes further progress in waste inertization desirable.

In this context, conversion of ash into stable, homogeneous silicate glasses should be especially interesting as the production of usable glass ceramics would allow that the

costs of the high-temperature processes could be partly offset. In practice, sinter-crystallization of combustion residues has the dual advantage of combining lower heating temperature with reduced volatilization losses. Although many processes are still at the laboratory stage, vitrification of fly ash or asbestos are already commercially used. In parallel, interest is being paid to using MSWI residues as sources of economically valuable materials. Dry discharge of bottom ash has, for example, been developed to optimize recycling of ash particles. Likewise, various concepts are tested to recover metals, taking, for instance, advantage of the fact [5] that heavy metals are preferentially incorporated in the opaque glasses of the MSWI residues, which form at combustions temperatures between 1000 and 1400 °C.

In all applications, however, risk assessment remains of great concern to government and society. In most countries the reuse of residues such as bottom ash is currently regulated on the basis of leaching tests whose results are in turn valuable to optimize the chemical compositions and fabrication processes of these materials. The use of various kinds of incineration ash for roads, pavements, embankments, or construction materials is now critically assessed to reduce the diffusion of toxic elements in the environment to harmless levels.

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9.11

Nuclear Waste Vitrification

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1 Introduction

In its quest to deal with radioactive waste, the nuclear industry has found glass to be a durable material for stabilizing even the most radioactive waste in the solid state. This solution is now acknowledged to be the most suitable for immobilizing the radioactive products arising from the fission of uranium or plutonium in nuclear reactors. The disordered structure of glass makes it possible to incorporate the multiple species contained in high-level nuclear waste. Glass compositions formulated for this type of application must comply with complex specification requirements designed to reconcile several objectives: to maximize waste loading in the glass in order to minimize the final volume of the vitrified wasteform, to guarantee the quality of containment over the lifetime of the radionuclides it incorporates, and to fabricate them at an industrial scale in radioactive environments. The success with which researchers and engineers have met these challenges during the last decades has made it possible to pass to the stage of industrial operations in most countries exploiting nuclear energy. In addition, much work has also been made to address the legitimate issue of the long-term stability of vitrified waste under geological conditions. This chapter thus describes the historical milestones of nuclear waste vitrification, the key issues related to nuclear glass formulation, the knowledge acquired on the long-term stability of waste glasses, industrial vitrification plants operated for their fabrication, and finally the issue of long-term stability.

2 History of Nuclear Waste Vitrification

Fission product solutions began to accumulate after the Second World War in all countries where nuclear fuel was reprocessed for defense purposes (USA, USSR, UK, and France). Subsequently, high-level waste (HLW) solutions containing fission products were also produced through reprocessing of spent nuclear fuel. The countries that developed a nuclear industry and undertook reprocessing for commercial and military applications were the United States, Russia, the United Kingdom, France, China, and India. Germany and Belgium also began commercial reprocessing, but later stopped their programs. Japan is currently developing a complete fuel cycle including spent fuel reprocessing. An estimate of the waste quantities involved is presented in Table 1. A fraction of HLW generated by reprocessing of civilian spent fuel has been vitrified but the cumulative radioactivity immobilized in these HLW nuclear glasses, estimated at $35.4 \cdot 10^7$ TBq in 2012, is significantly higher than the estimated $7 \cdot 10^7$ TBq [1] of cumulative defense HLW. However, the volume of HLW nuclear glasses already produced is significantly lower than the HLW generated by defense programs that is mostly stored in liquid form.

In fuel cycles involving reprocessing, fission products account for only 5 wt % of the spent fuel but are the source of about 98% of the total radioactivity. Whereas energy production from the remaining 95% recoverable elements (uranium, plutonium, or even minor actinides) is a challenge for recycling spent fuel, reprocessing also recovers solutions containing fission products, which constitute the ultimate waste from nuclear power. These highly radioactive and very complex solutions containing some 40 chemical elements must be cooled and often continuously stirred to dissipate more efficiently their thermal power. Maintaining the waste in the liquid state

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Table 1 Spent fuel and HLW inventory data.

Cumulative amount of civilian spent fuel (MTHM ^a) [1]		Amount of civilian spent fuel generated per year (MTHM ^a)	
Non reprocessed (2005)	Reprocessed (2002)	Estimated glass volume generated (m ³) if HLW is vitrified after reprocessing	Estimated defense and weapons HLW (m ³) [1]
185 000	85 000	12 000 ^b 120 ^c	8·10 ⁵

^a Metric tons of heavy metal.

^b Assuming a typical value of 0.2 TWh of electricity per MTHM and a world electricity production of 2600 TWh for the year 2010.

^c Assuming a typical value of 0.1 m³ of glass per MTHM.

was not a sustainable option, however, so that research was undertaken to confine the activity in a solid material as inert as possible. The objective was to develop a compact material capable of incorporating the radionuclides from these solutions and of limiting the release of activity in contact with vectors capable of transporting them to the human environment, especially through the corrosive action of water.

Be they glassy, crystalline, or composite, many materials have been investigated since the 1950s. With the implementation of industrial applications, however, glass has emerged over the years as the benchmark solution for durable confinement of the waste arising from reprocessing spent nuclear fuel. Glass has the advantage of incorporating most of the oxides contained in fission product solutions. Glass in addition provides homogeneity and flexibility for use with a range of Fission product solutions and can be fabricated at an industrial scale in radioactive environments. Crystalline materials such as Synroc have also been considered because they exhibit an even better chemical durability than that of glass. But they often come up against limits for the incorporation of fission products, as in the case of feldspar or mica tested during the 1950s, and also raise difficulties related to radionuclide partitioning between different phases, resistance to amorphization of glass-forming phases under irradiation, and implementation at the industrial scale.

In the 1950s at Chalk River, Canada, a radioactive waste solution was immobilized by incorporation at 1350 °C in a nepheline syenite (an Al₂O₃- and alkali oxide-rich rock) to which lime (CaO) was added. In France, the first radioactive glass was synthesized in 1957 at a laboratory scale at the Fontenay-aux-Roses site, and then at a larger scale (10 kg) at Marcoule in the 1960s with a sol–gel process. Other processes were tested at the same time in the United States at Richland in the Waste Solidification Engineering Prototype (WSEP) and in the United Kingdom at Harwell with the Fixation IN Glass of Active Liquors (FINGAL) process. By 1969, the PIVER semi-industrial scale pilot at Marcoule was used to vitrify fission product solutions produced by reprocessing spent

gas-graphite reactor fuel (1969–1973) and subsequently fuel from the Phenix fast neutron reactor (1979–1980). This was a batch process in which all the operations were carried out in a single furnace. In these semi-industrial pilots, glass batches were directly melted in a metallic canister (FINGAL) or in a furnace and then poured in a canister (WSEP, PIVER).

In France, such an achievement opened the way for industrial development (Figure 1), which began with the Marcoule vitrification facility (AVM) commissioned in 1978. In the 1980s, Russia and India also built industrial vitrification facilities in relation with their nuclear program, and the PAMELA process supported the cleanup program in Belgium. In the early 1990s, France and the United Kingdom commissioned the industrial vitrification facilities R7 and T7 at La Hague (Normandy) and WVP at Sellafield (Cumbria), respectively. In the same decade, the United States initiated a defense waste vitrification program at the Savannah River site (South Carolina) and cleanup operations in the civilian reprocessing facility at the West Valley site (New York). In Japan, the Tokai vitrification facility marked the beginning of Japanese operating experience in 1995 which is now applied at the Rokkasho site (North of Honshū). In Germany, the WEK vitrification facility was operated for nine months in Badewurtemberg in 2009–2010 for high-level liquid-waste treatment in the Karlsruhe cleanup program. In France, the first cold crucible melter was implemented in 2010 in the R7 facility at La Hague for new high-level liquid-waste treatment. This melter enables vitrification to be extended to a wider composition range of liquid waste.

3 Nuclear Glasses

3.1 Selection Criteria for Glass Formulation

The specification for the chemical composition of a containment glass represents a trade-off between three main objectives: satisfactory long-term resistance, chemical

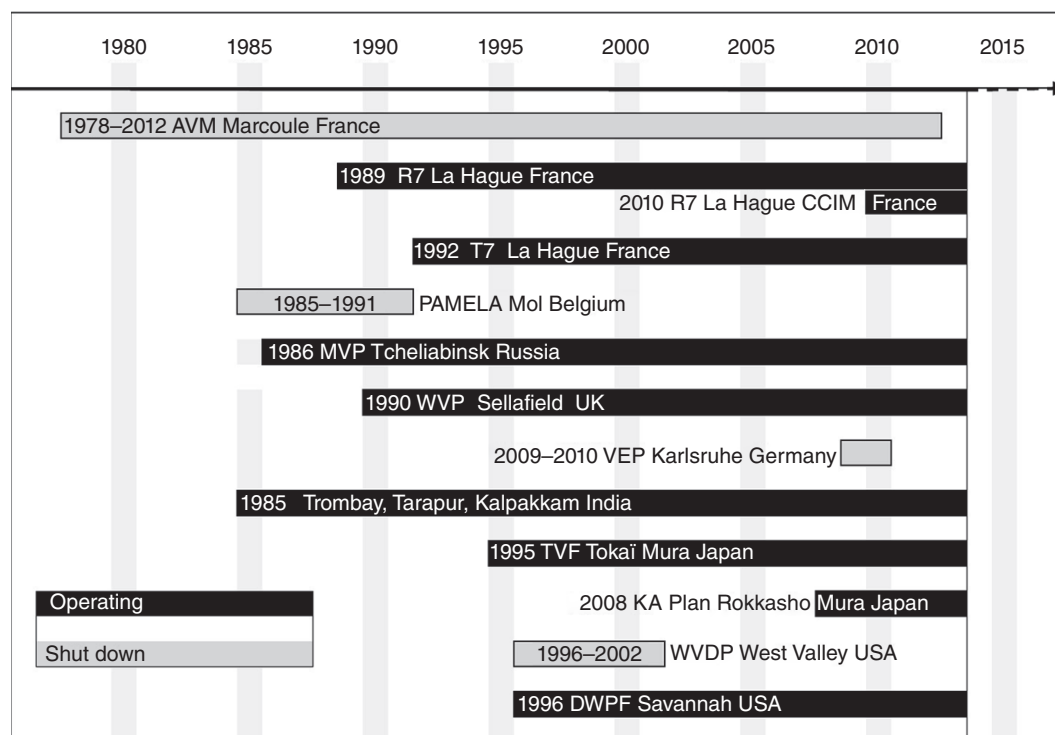


Figure 1 Operation of industrial vitrification plants around the world.

flexibility ensuring the incorporation of dozens of chemical elements in the glass structure at the atomic scale, and feasible implementation by an industrial process.

The nature and quantity of the waste must also be taken into account in this trade-off. Both the radiotoxicity of the containment glass and the thermal power emitted depend on the concentrations and half-lives of the radionuclides loaded in the glass. Radioactive wastes are classified into several categories, namely high-, intermediate-, and low-level waste [1]. HLW contains fission products and minor actinide elements arising from the burnup of uranium or plutonium fuel. It can be vitrified after separation from the spent fuel in a reprocessing plant and can thus immobilize more than 95% of the total radioactivity generated by nuclear power plants. Intermediate-level waste (ILW) arises from decontamination and cleanup operations, and contains long-lived radionuclides for which geological disposal is envisaged, as for HLW. It is less radioactive than HLW and emits less thermal power. Low-level waste (LLW) contains limited quantities of long-lived radionuclides and needs to be kept out of reach for a few hundred years.

It follows from these considerations that HLW must be confined in a matrix with greater long-term resistance than those intended for the other waste categories [2]. Glass was thus selected first as containment matrix for

HLW because of its ability to incorporate a wide range of elements in its structure. The three criteria pertaining to the long-term use of nuclear glasses concern their stability with respect to the radioactivity emitted by the waste they contain, to corrosion by groundwater in a geological repository, and to the temperature rises induced by the thermal power of the radioactive elements.

Another factor in the choice of a glass formulation is waste loading in the glass, i.e. the mass fraction of mineral species in the initial waste that is incorporated into the net mass of glass. It determines the required glass volume, which is often small in comparison with the initial waste volumes. Waste loading is often limited by the formation of secondary phases in the glass melt during synthesis or cooling. The glass compositions, waste loading, and synthesis temperatures are therefore modulated according to the solubility of the elements contained in these secondary phases. In this regard, depending on the waste composition, molybdenum, rare earth elements, aluminum, and transition metals such as chromium, iron, and nickel have been identified as primary species that limit HLW waste loading at around 20 wt % [3]. Loading limits associated with thermal power release must also be taken into account for the disposal of HLW (Table 2).

The selected commercial vitrification process itself also constrains glass formulation. It determines the conditions

Table 2 Thermal power of R7T7 glass from α , β , and γ emitters over time (W/L glass).

Years after vitrification	α	$\beta\gamma$
1	0.82	14.2
10	0.65	6.8
100	0.22	0.8
300	0.15	0.008
1000	0.05	0.0002

under which the initial waste is blended with additives, the possible temperature range of synthesis, the expected reaction rates, and their related uncertainties. These conditions also determine the viscosity of the melt at the process temperature, which ranges from a few tens to slightly more than 10 Pa.s. In addition to their composition, the physical nature of chemical additives is subject to optimization. Premade base glass is often used. It minimizes off-gas volumes and process time insofar as it is not too refractory. But glasses must also be formulated to prevent unwanted phenomena from taking place upon melting. An example is foaming caused by redox reactions in which elements such as cerium and iron may participate depending on their content and the oxidizing conditions of the melting process. One must also control the settling of non-solubilized particles by adjusting the melting temperature above the liquidus to prevent crystal formation or by limiting the addition of waste containing insoluble noble metals and other elements that could form alloys with them, such as tellurium. The glass formulation must also be compatible with the heating mode in terms of suitable electrical and thermal properties in the melt (Chapter 1.3). The waste activity level also influences the operating procedures. Minimizing the process maintenance requirements is particularly important for the vitrification of HLW; in some cases, this criterion may favor glass formulations synthesized at lower temperature to limit corrosion and volatility.

For radioactive waste immobilization, borosilicate systems have been selected as the reference matrix compositions for HLW in most countries because they represent the best compromise between these various constraints. With silicon and boron as the main network formers, together with alkali and alkaline earth network modifiers, they represent a good trade-off by ensuring the required chemical durability of the final glass and a process temperature of around 1100 °C. Aluminum is added to the HLW solutions to ensure their satisfactory calcination and also to ensure a good homogeneity of the glass.

Alkali phosphate glass was alternatively used in Russia before the turn of the century; over borosilicate glass, it

had the advantage of lower synthesis temperatures of about 1000 °C and could better solubilize sulfates, a point which, however, is still under discussion. But this type of glass is no longer used because of its low chemical durability and significant corrosiveness, and it has further lost its appeal because of a change in reprocessing methods that no longer produce high-level solutions rich in sulfates [4]. Lead iron phosphate and iron phosphate formulations were also proposed for this purpose, but did not result in industrial-scale processes. For lower activity waste, aluminosilicate glass formulations have also been used, notably for vitrification processes at very high temperatures (>1300 °C) designed to immobilize a range of lower-level radioactive wastes [5] or other toxic wastes [5].

3.2 Nuclear Containment Glass Properties

Reprocessing of current nuclear fuel typically yields about 40 kg of fission products and minor actinides per metric ton of reprocessed uranium. The fission product and minor actinide waste streams are supplied to the vitrification process as a nitric acid solution, and must be dried and calcined before being incorporated in an oxide matrix. Depending on the process, this transformation is performed either in a preliminary step before vitrification or directly on the surface of the molten glass. In either way the fission product solutions (Table 3) become complex oxide mixtures that contain no glass network formers in appreciable amounts. Hence, incorporation of these chemical species in an oxide glass requires addition of network-forming and network-modifying oxides.

Table 3 Composition of reference fission product solution vitrified in R7 and T7 facilities at La Hague (g/L).

Element	g/L	Element	g/L
Na	14.09	Cs	3.72
Al	3.52	Ba	2.21
P	0.51	La	1.7
Cr, Fe, Ni	11.22	Ce	3.3
Rb	0.5	Pr	1.56
Sr	1.18	Nd	5.63
Y	0.65	Pm	0.1
Zr	6.48	Sm	1.12
Mo	4.7	Eu	0.18
Tc	1.16	Gd	0.11
Ru, Rh, Pd	5.48	U	0.11
Ag, Cd, Sn, Sb, Se	0.38	Pu	0
Te	0.67	Am, Cm, Np	1.08

These glass-forming additives are generally supplied as raw materials, glass flakes, or glass beads mixed with waste either before vitrification or simultaneously with the waste into the melter to minimize the off-gas volume and process time. A high-level nuclear waste containment glass consists of about 70–80 wt % of inactive oxides, known as vitrification additives (mainly SiO_2 , B_2O_3 , Na_2O , and Al_2O_3 in the case of borosilicates). Vitrification at an industrial scale must allow for possible composition variations resulting from uncertainties in the processes and waste composition. Fission product containment formulations are oxidized glasses where $\text{Fe}^{2+}/\text{Fe}^{3+} \ll 1$. Various borosilicate glass formulations (Table 4) have been developed to accommodate the variety of elements present in high-level nuclear waste. Their variations reflect differences in the nature of the fuel and the reprocessing process implemented and also differences in the composition of the solutions of fission products derived from nuclear materials generated by older processes developed for defense programs.

Glass formulations that give rise to homogeneous microstructures are preferred for HLW containment glass to make their industrial production easier and modeling of their long-term stability more reliable. Industrial HLW glass generally contains crystalline phases with a volume fraction of a few % at most, which results from partial devitrification upon cooling at temperatures below 900 °C. The most common crystalline phases are spinels $[(\text{Ni},\text{Zn})(\text{Cr},\text{Fe})_2\text{O}_4]$, mixed cerium and zirconium oxides, powellite (CaMoO_4), and rare earth silicates such as $\text{Ca}_2\text{Nd}_8\text{Si}_6\text{O}_{26}$ [3, 6]. In addition to these crystals, Pd,

Rh, Te metal particles and RuO_2 precipitate because the platinum group metals present in fission product solutions are not soluble in the borosilicate melt (Figure 2).

In some instances, radioactive waste has nonetheless been immobilized at an industrial scale in glassy matrices with a more complex microstructure. This has been the case in France at La Hague for high-activity UMo glass containing up to 12 wt % molybdenum in a glass-ceramics fabricated by melting (Figure 3), and in Switzerland at Würenlingen for glass matrices designed to confine LLW residues that may include crystallized and metallic phases after heat treatment.

The main physical characteristics of R7T7 nuclear waste glasses produced at La Hague are indicated in Table 5.

4 Long-Term Stability of Nuclear Glass

4.1 Glass Waste Storage Context

Nuclear waste glass is an amorphous, dense, and generally homogeneous material containing tens of oxides. Upon cooling, its temperature reaches T_g a few hours after pouring in the canister. Then glass undergoes cracking, which significantly increases its reactive surface area. The canister storage is designed to maintain the glass temperature significantly below T_g in spite of the heat produced by radioactive disintegrations. The fate of the

Table 4 Composition of nuclear waste containment glasses (wt %).

	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	Fe_2O_3	P_2O_5	ZnO	Li_2O	MoO_3	ZrO_2	MgO	Other
<i>France</i>													
Average R7-T7 glass	45.6	14.1	9.9	4.7	4.0	1.1	0.2	2.5	2.0	2.2	2.8	–	10.9
Ref. UMo glass-ceramic	38.7	13.9	9.4	7.1	6.1	0.3	3.1	6.0	0.2	10.0	3.3	0.1	1.8
<i>Germany</i>													
Simulated GP WAK1	50.4	14.8	10.3	2.6	4.5	1.9	0.4	0.0	2.9	0.9	0.7	1.8	8.8
<i>Japan</i>													
Simulated P0768 glass ^a	46.6	14.2	10.0	5.0	3.0	2.0	0.3	3.0	3.0	1.5	1.5	–	9.9
<i>UK</i>													
Nominal Magnox glass	47.2	16.9	8.4	4.8	0.0	2.4	0.2	0.0	3.4	1.6	1.6	5.3	8.2
Blend glass	46.3	15.9	8.6	1.6	0.0	1.1	0.1	0.0	3.9	2.2	2.8	1.4	16.1
<i>US</i>													
DWPF startup reference glass ^b	49.0	8.8	11.5	4.7	1.2	13.5	0.0	0.0	3.5	0.0	0.0	0.7	7.1

^a TVF surrogate glass.

^b Typical composition of DWPF glass.

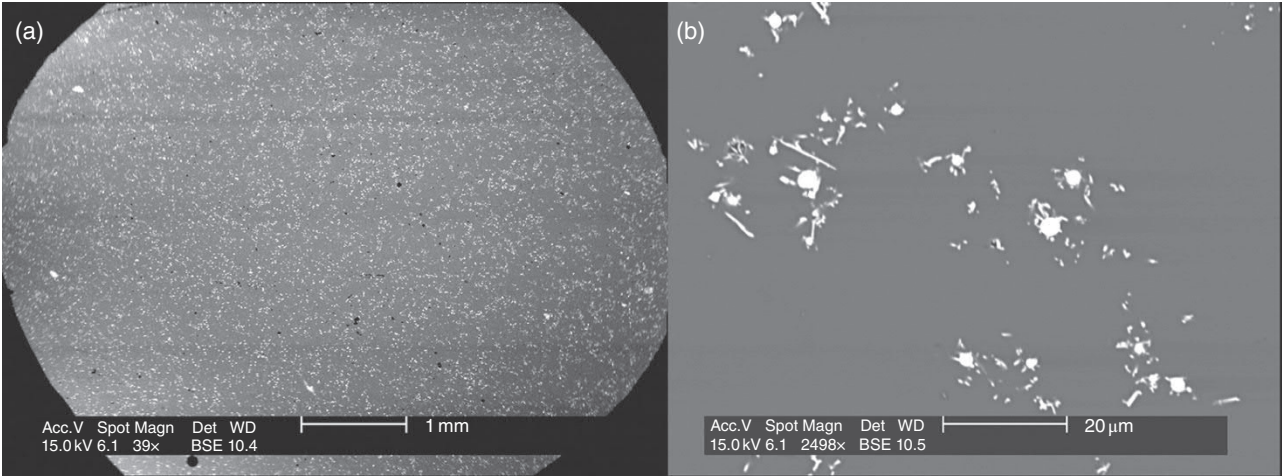


Figure 2 Pd-Te (spherical) and RuO₂ (needle-shaped) metallic precipitates undissolved in R7T7-type high-level waste glass as seen as small particles with high electron contrast at two different scales in scanning electron microscope images. (a) Overall view and (b) detailed view. Source: CEA.

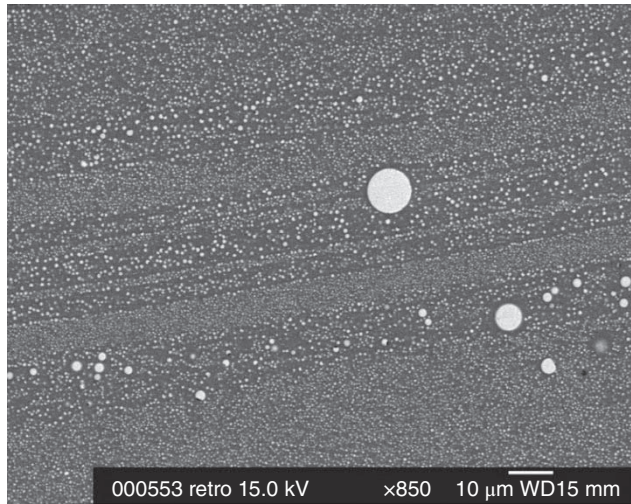


Figure 3 Partially crystallized beads enriched in molybdenum, phosphorus, and calcium seen as light-colored inclusions in the (dark) encapsulating borosilicate glass of the UMo glass-ceramics. Source: Scanning electron microscope image from CEA.

Table 5 Physical properties of R7T7 glass.

293–573 K thermal expansion coefficient	8.3·10 ^{−6} /K
Thermal conductivity (373–773 K)	1.0–1.3 W/m·K
Specific heat capacity (298–773 K)	0.8–1.2 J/g·K
Density (298 K)	2.62–2.84 g/cm ³
Viscosity (1373 K)	8–14 Pa·s
Glass transition temperature (<i>T_g</i>)	773–806 K

existing and future glass canisters is intimately related to the disposal concept. The question of safe management of HLW has been debated for decades and has converged on deep geological disposal. Moreover, it is acknowledged worldwide that a multiple-barrier design is the safest way to ensure low corrosion rates of wasteforms and the slow migration of radionuclides through the geosphere in case of canister degradation. As a consequence, demonstration of safety directly relies on the ability to predict accurately the source term (i.e. the flux of radionuclides released from the glass over time) and the fate of radionuclides in the geosphere and potentially in the biosphere for periods of up to 10⁶ years.

From a scientific point of view, calculating possible release of radionuclides is difficult because glass is a thermodynamically metastable phase, which, upon alteration by groundwater, undergoes an irreversible kinetically limited transformation into more stable phases. A robust answer to the stability issue requires a deep understanding of the mechanisms of the glass/water interaction from which a mathematical model can be derived. Modeling is necessary as glass durability depends on many parameters (such as temperature, pH, glass composition, radioactivity, the renewal rate of the contacting fluid, etc.) on different time and distance scales [7].

4.2 Chemical Durability of Glass

Whatever the glass composition and the alteration conditions, several interrelated processes can take place at the glass surface during corrosion: water diffusion, ion exchange between hydrogenated species and alkalis

weakly bonded to glass formers (also called interdiffusion), hydrolysis of covalent and ionic-covalent Si–O–M bonds (M = Si, Al, Zr, Fe, Zn, etc.), condensation of more or less detached species from the glass surface, and precipitation of crystalline phases from amorphous phases and soluble species. Nuclear glasses are dense materials in which water diffuses slowly: the effective diffusion coefficient of water typically ranges between 10^{-17} and 10^{-23} m²/s⁻ depending on temperature (25–90 °C), pH (3–10), and glass composition. As a result, corrosion of such materials is generally seen as a surface reaction from macroscopic to microscopic scales.

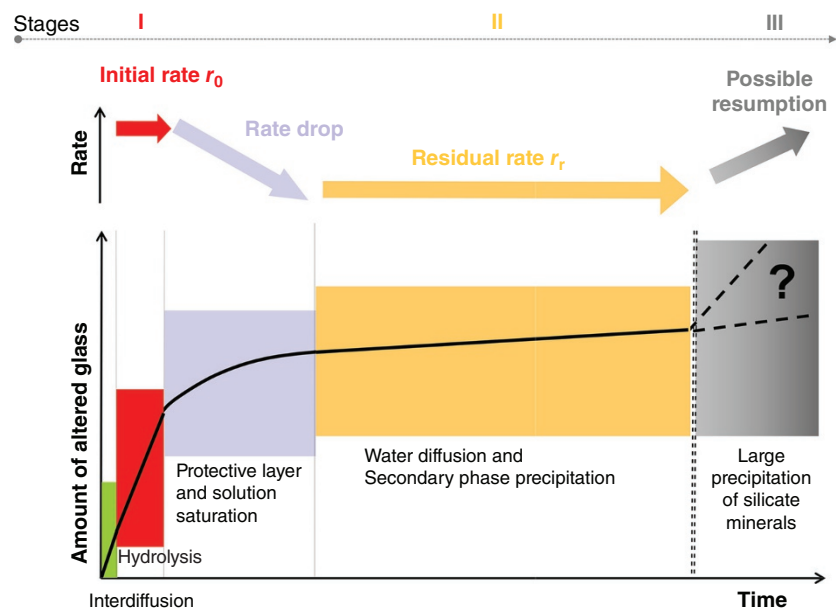
Depending on glass composition as well as on chemical and physical conditions near the glass surface, these mechanisms can contribute to or control the apparent dissolution rate, which is generally measured by the release of mobile species into the bulk solution. If their solubility is high, the glass components – including the radionuclides – remain dissolved in the solution. If not, they either remain at the glass surface to form an amorphous, porous, hydrated material called the gel layer (cf. Chapter 5.12), or they precipitate into stable crystalline phases (generally located at the surface of the gel).

Under conditions representative of geological disposal environments, the aforementioned mechanisms can be linked to three main stages of corrosion [7]: (i) the initial rate, (ii) the residual rate, and, in some cases, (iii) the resumption of relatively rapid alteration (Figure 4). For several reasons the “interdiffusion” step and the “rate drop” shown in Figure 4 are not considered as formal kinetic stages. Interdiffusion takes place at each of these kinetic stages but acts alone only for a very short time.

The rate drop simply represents a transition between the initial and residual rates accompanied by the progressive saturation of the solution with respect to silica and by the formation of various surface layers that could impact continued corrosion. There is general agreement that the initial dissolution rate is controlled by the hydrolysis of Si–O–M bonds, whereas the debate remains open concerning the mechanisms limiting the residual rate [8]. The mechanisms considered are the slow transformation of amorphous phases into more stable products, changes in the local solution concentration (especially the concentration of silicon), water diffusion into the glass, or transport limitations in a passivating layer. As a matter of fact, several of these mechanisms seem to compete but there is no consensus on their relative importance or mutual relationships [9]. The potential for the resumption of relatively rapid alteration appears to depend on a combination of glass composition and environment, particularly at high temperatures and/or in very alkaline solutions. Zeolites are the main type of minerals responsible for this phenomenon by consuming Si and Al released by the glass, such phases precipitate at the expense of the passivating layer.

The design of multiple-barrier systems – i.e. the nature and amount of materials placed between the glass and the host rock – is expected to affect strongly both the mechanisms and rate of glass corrosion (the latter typically ranging from tens to several hundreds of μm/year at 90 °C, depending on glass composition). For example, a concrete overpack, as in the Belgian design, emphasizes the protection of the overpack material through the engineering of a high-pH environment. Once the overpack is

Figure 4 Summary of the distinct stages of nuclear glass corrosion and related potential rate-limiting mechanisms. The duration of each stage depends on the glass composition and leaching conditions (temperature, pH, solution composition, renewal rate, etc.).



breached, however, this environment could maintain the glass in stage (i) or (iii), thanks to the precipitation of calcium-silicate hydrates and zeolite, as long as the composition of the pore water contacting the glass is fixed by concrete. Conversely, an environment with a lower pH and a low groundwater renewal rate, as in the current French or Japanese design, would allow the glass to be altered in stage (ii), leading to much lower glass corrosion rates, although recent findings indicate that the presence of iron (from the overpack) in the vicinity of glass could sustain glass corrosion at higher rates for a longer time than previously expected. In the concepts relying on a durable glass, it becomes of primary importance to improve our knowledge of the mechanistic controls behind both stage (ii) and stage (iii) alteration. This suggests a focus on water transport and aqueous species reactivity in nanoporous materials (hydrated glass and gel), monitoring of slow kinetics, and a better understanding of the nucleation and growth of stable crystalline phases. A common fundamental understanding in these areas will lead to improved mechanistic models, which will eventually take into account the rate sensitivity to the glass composition and the environmental conditions.

The predictability of the models is evaluated through dedicated integrated tests performed in the laboratory or in underground research laboratories (Mol in Belgium, Mont Terri in Switzerland, Bure in France) and by analogy with natural and archeological glass specimens [10]. The latter materials provide a unique means to verify the rate-limiting mechanisms that control glass alteration over a geological timescale in natural environments. Numerous results supporting current models have been obtained in recent years through investigations of Roman glass blocks altered in seawater, slag buried in clay from an archeological ironmaking site, the so-called chondrite meteorites, basaltic glasses altered in various environments, etc. [9].

4.3 Effect of Self-Irradiation

Among the different sources of radiation within HLW glasses (Chapter 3.13), recoil nuclei from α emitters are the main cause of structural changes and variations of glass properties such as density, Young's modulus, microhardness, etc. The problem is to determine to what extent the confinement properties of the glass are affected over time by self-irradiation. This question has spurred experimental and theoretical work for at least the last two decades. Borosilicate glasses have been found very tolerant to the different sources of irradiation because self-healing processes allow fast reconstruction of local damage [11]. At high doses, typically around 10^{18} α decays/g, most of the glass properties reach a steady state. Moreover, the slight evolution of the macroscopic properties observed

up to the threshold indicated above (for R7T7-type glass, the 0.5% density decrease, the 20–30% decrease of Young's modulus by 20–30%, and the 50–100% increase of fracture toughness) have been explained in terms of structural changes, thanks to material characterization at an atomic scale and molecular dynamics simulations. A connection between these changes and the fictive temperature has been established from an analogy between the effects of both ballistic damages and the quenching rate on the glass structure. Concerning the production of He by α decay, it has been shown that the rate of helium loss by diffusion should be fast enough to avoid the formation of gas bubbles.

But these reassuring answers cannot be easily generalized to glass-ceramics as it is known that certain crystals swell much more than homogeneous borosilicate glass. This feature could lead to internal stress and the formation of cracks, thus increasing the reactive surface area.

Another issue is still under consideration. Does radiolysis affect glass durability, especially under the residual rate regime which is expected to be actually relevant in the geological repository? Although preliminary results do not show significant differences in residual rates between inactive samples and α - or β -doped glass samples, a better understanding of the potential effects of irradiation on alteration mechanisms under irradiation is required to confirm these results.

4.4 Thermal Stability

From a theoretical standpoint, glass is a metastable phase that could evolve toward a more organized state over long periods of times (Chapter 3.3) through crystal nucleation and growth or transport of reactive species within the glass itself. It is known that below T_g , transport is rate-limiting and glass crystallization is very slow, even if one considers the timescale of geological disposal of nuclear glasses. Experimentally, accelerated tests have been conducted to determine the type of crystals that could form in nuclear glasses and the maximum potential fraction of crystals. Cerium oxide, spinels like ZnCrO_4 , powellite, and Si-bearing apatite are major phases reported in the literature that have been observed during heat treatment of borosilicate glasses of nuclear interest. In the case of R7T7 type glass, the maximum crystal fraction should not exceed a few volume %. This suggests that even if crystals were forming, they should not affect the confinement properties.

4.5 Conclusion About the Long-Term Stability of Nuclear Glass

Thanks to multidisciplinary research performed in recent decades, remarkable progress has been made on the issue

of radionuclide waste storage, which allows us to draw the following conclusion: nuclear glass canisters, if placed in a suitably designed environment could last several million years and thereby significantly limit the release of radionuclides toward the geosphere. Because glass properties are very sensitive to many factors, however, inappropriate environmental parameters such as a high pH or a high groundwater flow rate could drastically reduce the glass life time. In scenarios under development in the world, great care is thus taken to select very confining host rocks and to design efficient engineered barrier system that would guarantee a very low release of radionuclides from the vitreous matrices.

5 Industrial Implementation of Nuclear Waste Vitrification

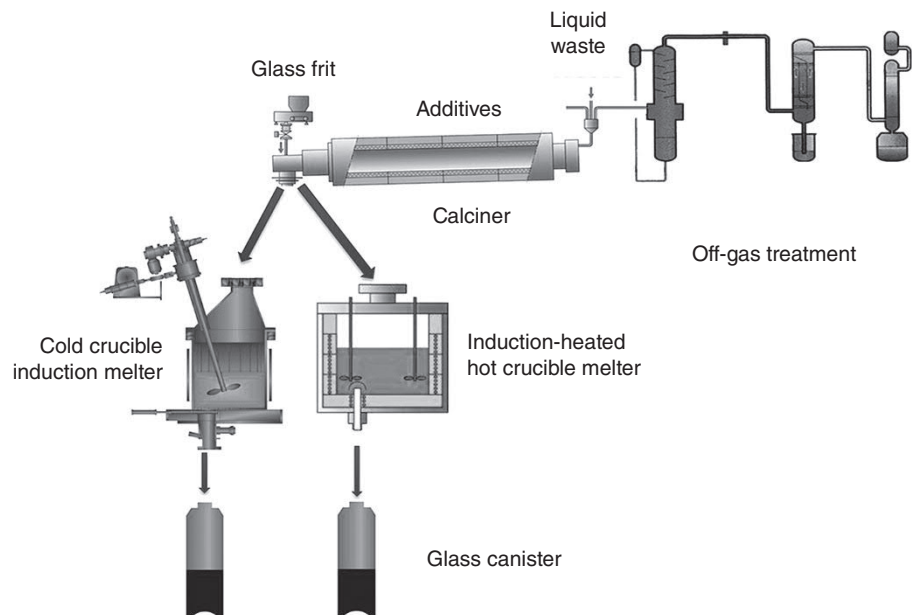
The fission product solutions are incorporated into vitrified waste packages by the following main operations: evaporation of water; thermal conversion of chemical elements to oxides; production of glass after addition of a glass additives to form a borosilicate by melting in a furnace between 1050 and 1300 °C; pouring into canisters; cooling to produce a solid glass; and sealing of the canister. The fission product feed solutions are highly radioactive so that the vitrification processes must be carried out in shielded cells. Electrically heated melters are used to comply with safety and remote maintenance requirements.

5.1 Industrial Processes

Vitrification processes based on two distinct technologies have been developed around the world. With the first, vitrification is carried out in two steps in separate devices, the first for evaporation and calcination, the second for glass preparation and melting. Fission product solutions, as well as reagents and solutions recycled from the off-gas treatment system, are fed to the calciner, a rotating tubular kiln heated by a resistance furnace (Figure 5). Calcining results in evaporation of the solutions and partial conversion of the nitrates to oxides. The calcine from the rotating kiln falls into the melter together with the glass frit necessary to form the containment glass. Then the glass can be produced either in a metal melting pot induction-heated at 4 kHz to a temperature of about 1100 °C, or in a cold crucible melter where the melt is heated by induction at 300 kHz to about 1250 °C. The chemical and thermal homogeneity of the product is achieved by means of mechanical stirring and bubble-stirring by gas injection. The glass is poured in batches into stainless steel canisters containing about 400 kg of glass. After lid welding and external decontamination, the canisters are transferred to an interim storage unit. These technologies have been chosen in order to separate the process functions, to implement simple, compact technologies in which all the components are interchangeable for ease of use in a high-activity environment, and to facilitate upgrades in industrial facilities.

With the second process, vitrification is continuously performed. The feed solution is introduced directly into

Figure 5 Two-step vitrification process of nuclear waste with either “cold” (left) or “hot” (right) crucible melters.



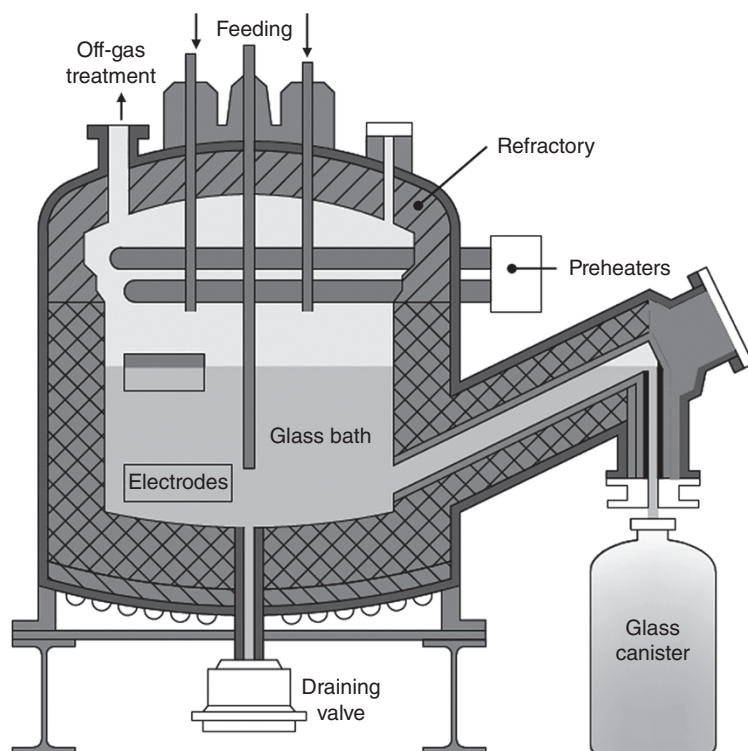


Figure 6 Sketch of an LFCM liquid-fed ceramic melter equipped with a bottom drain valve and an overflow pouring spout.

the melter where the water is evaporated and the elements are converted to oxides on the surface of the melt (Figure 6). A reducing agent is sometimes added to the feed solution to control the redox potential of the molten glass in the melter. Glass frit or glass-forming chemicals are supplied to the melter at the same time as the vitrification feed solution to form the glass network. Glass additives or chemicals are added either in solid form or as a slurry in suspension in the feed solution. The glass forms on the surface of the melt. The liquid-fed ceramic melter (LFCM) or Joule heated ceramic melter (JHCM) is lined with refractory material consisting of zirconia, alumina, and chromium oxide. The melt is heated to 1150–1200 °C by an electric current flowing between water-cooled metal electrodes embedded in the refractory furnace walls. The glass can be poured into canisters continuously by overflow through a siphon or in batches through a thermal valve at the bottom of the melter. After lid welding and external decontamination, the canisters are transferred to an interim storage unit. The melting furnaces are generally massive refractory assemblies that allow very stable operation over their lifetime of between 5 and 10 years. At the end of its service, life the melting furnace is difficult to replace so that it constitutes a very bulky secondary waste item.

5.2 Industrial Vitrification Facilities for High-Level Liquid Waste Around the World

The main features and operating data for the industrial-scale high-level liquid waste (HLLW) vitrification facilities in each country are summarized in Table 6.

5.2.1 France

Three industrial vitrification facilities implementing the two-step vitrification process (calcining and glass melting) have been built in France.

The Marcoule vitrification facility (AVM), operated in conjunction with the UP1 reprocessing plant at Marcoule, had a calciner with an effluent evaporation capacity of 40 L/h and an induction-heated melter containing 150 kg of molten glass and capable of producing 18 kg of glass per hour. This facility was operated from 1978 to 2012.

The other two facilities, R7 and T7, are located at La Hague. The former, associated with the UP2-800 reprocessing plant, was commissioned in 1989. The latter, associated with the UP3 reprocessing plant, was then commissioned in 1992. Both include three vitrification lines, originally with a calcining unit which is a 4-m length rotating kiln, with a capacity of 76 l/h improving to 90 l/h and an induction-heated melter. It is an ovoid melter

Table 6 Summary of characteristics of high-level waste vitrification facilities (2012 data).

	Melting process	Pool surface area m ²	Operating period	Produced glass mass MT	Number of canisters	$\beta\gamma$ activity $\times 10^6$ TBq
<i>France</i>						
AVM Marcoule	IHCM	–	1978–2012	1357	3306	22
R7–T7 La Hague	IHCM	–	1989–	6555	16 885	262
R7 La Hague	CCIM	–	2010–	76	190	–
<i>UK</i>						
WVP Sellafield	IHCM	–	1990–	2200	5615	33
<i>USA</i>						
WVDP West Valley	JHCM	2.3	1996–2002	570	275	0.9
DWPF Savannah River	JHCM	2.6	1996–	6300	3591	1.8
<i>Russia</i>						
Mayak	JHCM	10	1987–	8000	–	33
<i>Belgium–Germany</i>						
PAMELA Mol	JHCM	0.7	1985–1991	500	2201	0.5
VEK Karlsruhe	JHCM	0.44	2009–2010	55	140	0.8
<i>Japan</i>						
TVF Tokai-Mura	JHCM	0.7	1995–	70	241	–
<i>India (2008 data)</i>						
WIP Trombay	IHPTM	–	2002–	12	200	–
WIP Tarapur	IHPTM	–	1985–2002	–	690	–
AVS Tarapur	JHCM	1	2006–	10	100	0.15

IHCM, induction-heated hot crucible melter; IHPTM, induction-heated pot-type melter; JHCM, Joule-heated ceramic melter.

containing 300 kg of molten glass and producing 25 kg of glass per hour. In 2010, the melter in one of the three lines of R7 was dismantled and replaced by a cold crucible melter to vitrify “legacy” intermediate-level liquid waste. This melter contains 400 kg of molten glass and produces up to 40 kg of glass per hour.

5.2.2 United Kingdom

An industrial vitrification facility was built at Sellafield in the United Kingdom implementing the two-step (calcination and melting) vitrification process in an induction-heated melting pot. Associated with the MAGNOX and THORP reprocessing plants, the waste vitrification plant (WVP) was commissioned in 1990 and initially included two vitrification lines with the same characteristics as the French units at La Hague. A third line with similar performance began operation in 2004.

5.2.3 United States

Two industrial facilities have been built in the United States.

In the West Valley Demonstration Project (WVDP), a vitrification demonstrator was associated with a PUREX and THOREX reprocessing plant for commercial spent fuel operated from 1996 to 2002. The LFCM, with a surface area of about 2.2 m² heated by three electrodes (including one at the bottom of the furnace), had a capacity of 35 kg/h. The glass was poured off through an overflow spout. When the commercial reprocessing project was stopped, the vitrification facility was being operated for the treatment of liquid waste. WVDP is now being dismantled.

At the Savannah River Site, the vitrification unit of the Defense Waste Processing Facility (DWPF) was built to vitrify 130 000 m³ of sludge and effluents from the defense reprocessing plant. It began operating in 1996. It includes a LFCM with a surface area of 2.6 m², with a side-mounted siphon to fill the glass canisters and a drain valve at the bottom of the melter. The furnace weighs 65 tons and holds 6500 kg of glass. The first melter was operated industrially from 1996 to 2002. The second melter equipped with an argon bubble-stirring system

has been in operation since 2004 and will likely be replaced from 2014.

5.2.4 Russia

The vitrification facility associated with the RT1 plant in the P.A. Mayak complex at Chelyabinsk implements EP-500 side-pouring electrode melters with an evaporation capacity of about 500 l/h. The first melter was commissioned in 1987, and four melters have been operated successively since then.

5.2.5 Belgium

The PAMELA vitrification facility was operated from 1985 to 1991 at the Eurochemic reprocessing plant near Mol, Belgium. It was equipped with a LFCM having a surface area of 0.7 m², a flat bottom with a drain valve, and an overflow pouring spout actuated by an airlift. The furnace weighs 18 tons and holds 750 kg of glass. Two melters were used successively, and both failed due to the accumulation of noble metals and aluminum-rich phases at the bottom of the unit. They vitrified about 500 metric tons of glass in 2201 canisters containing a total activity of $0.5 \cdot 10^6$ TBq. PAMELA vitrification facility was stopped when vitrification of the liquid waste coming from Eurochemic reprocessing plant decommissioning was complete.

5.2.6 Germany

The VEK vitrification facility associated with the WAK pilot reprocessing plant at Karlsruhe was built to vitrify 60 m³ of legacy HLLW. It was equipped with a LFCM having a surface area of 0.44 m², containing 450 kg of molten glass, with several pairs of heating electrodes. In order to process effluents containing noble metals and prevent their accumulation, the bottom of the melter was inclined at about a 60° angle and the melt was poured through a metal tube at the bottom of the unit. VEK was operated for a single campaign from September 2009 to June 2010. It is now being dismantled.

5.2.7 Japan

The Tokai Vitrification Plant (TVF) associated with the Tokai Reprocessing Plant (TRP) has a 0.7 m² ceramic melter tapering downward at a 45° angle. The glass melt is poured from a metal tube at the bottom of the melter. The plant began operating in 1995. The first melter (TVF1) was operated in 1995–1996 and again in 2000–2002. The second melter (TVF2) was commissioned in 2004 and operated until 2007. A technological development program is now in progress to improve melter operation in the presence of noble metals.

5.2.8 India

Vitrification processes are implemented at India's two reprocessing sites, Trombay and Tarapur. At Tarapur, the Waste Immobilization Plant (WIP) has been in operation since 1985, initially with two vitrification units that used induction-heated metal melting pots operating in batch mode supplied directly with the feed solution and glass frit. These melters were dismantled and replaced by two new units comprising the Advanced Vitrification System (AVS) with two JHCMs of about 1 m². The first ceramic melter operated for six years, and the second was only recently commissioned. At Trombay, three vitrification units with induction-heated metal melting pots operating have been operated in batch mode, supplied directly with the feed solution and glass frit.

5.3 New Vitrification Projects

New HLW vitrification projects are currently in progress throughout the world.

- In Japan, the KA vitrification facility associated with the Rokkasho-Mura commercial fuel reprocessing plant is awaiting the startup of commercial operation. It comprises two 2.6 m² LFCMs with walls inclined 45° and hold about 4 tons of glass. The production capacity of each unit will be about 35 kg of glass per hour.
- In India, a vitrification facility implementing enhanced technologies is now in the process of final inspection and approval at Kalpakkam.
- In China, the China Vitrification Project is now in progress at Guangyuan, the facility has been designed with a LFCM having a glass production capacity of about 30 kg/h.
- In the United States, vitrification units are being built at Hanford for high- and low-level defense liquid waste. The HLLW vitrification facility will use a LFCM with a surface area of 3.75 m², and is expected to be commissioned around 2022.

Vitrification processes were originally developed to immobilize HLLW. Along with other processes, they are also used for intermediate- and low-level liquid effluents and sludges. In Russia, for example, SIA Radon has been operating a cold crucible melter since 1999 to vitrify intermediate- and low-level liquid waste, producing more than 30 metric tons of glass. A vitrification facility is now under construction at Hanford, in the United States. It will operate with two 10 m² ceramic melters heated by Joule effect electrodes with a unit production capacity of 10 tons/day. The two-step vitrification process is also implemented in a cold crucible melter in France at La Hague to vitrify ILW solutions arising from decommissioning operations.

Low- and intermediate-level combustible solid waste can be incinerated to destroy organic material, as the ashes are simultaneously vitrified in the melter. An example is the Ulchin vitrification facility in South Korea, commissioned in 2009 for the incineration and vitrification of waste from commercial nuclear power plants. The waste is incinerated on the surface of a molten glass bath in a cold crucible melter. The processing capacity of this unit is 20 kg/h.

In Switzerland, an incineration-melting-vitrification process has been operated since 2004 for Very low-level waste (VLLW) and LLW in a plasma arc centrifugal treatment (PACT) system using a rotating crucible with a 1200 kW transferred arc plasma torch. After burning the organics with the plasma torch, the ashes and metal waste remaining in the melter are melted and/or vitrified. The processing capacity of the facility can reach 200 metric tons of waste per year.

6 Perspectives

An international consensus is emerging about the long-term quality of the containment provided by immobilization of high-level nuclear waste in glass, with a preference for borosilicate glass formulations. The cost of spent fuel reprocessing including glass canisters production is estimated to be a few percent of the total production cost of electricity [12]. For economic or political reasons, however, reprocessing of spent nuclear fuel with vitrification of the HLW has not been adopted by all countries producing nuclear electricity. Future changes in the positions of these countries could contribute to increased production of nuclear containment glasses with improvements in the industrial performance of the processes, such as extended melter lifetimes and larger production capacities. In the coming decades, improved disposal concepts for vitrified waste packages can be expected together with their actual implementation after a preliminary experimental stage.

It is now envisaged to extend vitrification to a broader range of radioactive waste. Facilities have already been implemented to vitrify radioactive effluents arising from cleanup and remediation (France), to vitrify various low-level radioactive wastefroms including hospital waste or low-activity waste from nuclear power plants (Switzerland, Japan, South Korea). Vitrification projects based on plasma technology are being investigated around the world and could lead to industrial applications in the coming decades [13]. They concern the immobilization of a range of radioactive waste or sludge. In addition to treating radioactive waste, vitrification is also a possible option for the treatment of toxic waste such as asbestos or the fly ash from domestic waste incineration

(Chapter 9.10). A few commercial facilities of this type have emerged, but the advantages of these treatments have not yet offset their cost in the eyes of policy-makers, although their positions could change in the light of the increasing importance of environmental issues associated with waste management in general.

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9.12

The International Commission on Glass (ICG)

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1 Introduction: Origins of ICG and Founding Members

The International Commission on Glass is a unique body where experts from academia and industry meet to understand and solve practical and fundamental issues in glass science and production. Its roots lie in conversations in the 1920s between international glass experts, particularly Prof. William E.S Turner (1891–1963) [1] and Prof. Georg. R. Gehlloff (1882–1931). Prof. Turner was Head of the Department of Glass Technology in Sheffield, UK, and a Founding Member in 1916 of the Society of Glass Technology (SGT). Prof. Gehlloff was a Member of the Board of Directors of OSRAM in Berlin and Head of the Glass Laboratory at Weiswasser. He also represented the newly formed (1922) Deutsche Glastechnische Gesellschaft (DGG) based in Frankfurt am Main. Their societies arranged a joint conference in Aachen, a model for later ICG meetings (1928). They created technical committees to define terms and facilitate precision in the technical literature, standardize the methodologies for measuring thermal expansion, and test both chemical durability and refractivities.

Similar discussions were happening elsewhere (Figure 1). The SGT met with the Glass Division of the American Ceramic Society in 1920 and a reciprocal visit followed in 1928. Meetings with France and Belgium representatives took place in 1923 and 1924, respectively. After Gehlloff's untimely death (1931), Dr. H. Maurach, DGG Managing Director, continued with Turner to pursue the dream of extending such collaboration to other national organizations. Their aspirations bore fruit in 1933 when a formal document defining both a structure and aims was approved by six countries during the first

ICG Congress on Glass in Venice. Signatories were J. Antonio De Artigas (Spain), J. C. Hostetter (USA), B. Long (France), H. Maurach (Germany), A. Mauri (Italy), and W. E. S. Turner (England). Prof. Turner was its first President and Dr. Maurach its first Honorary Secretary. While World War II halted progress for a decade, the organization survived and has continued to grow. Its current status and activities will be reviewed in this chapter.

Acronyms

AC	Advisory Committee
CTC	Coordinating Technical Committee
EFONGA	European Forum on New Glass Applications
ICG	International Commission on Glass
MB	Management Board
NPO	National Participating Organization
SC	Steering Committee (used in early years for subcommittee)
TC	Technical Committee

2 ICG as an Organization

2.1 The Constitution

A formal constitution codifying those early dreams was not created until 1950, after formal discussions recommenced in 1948. The stated aims were *to promote and stimulate understanding and cooperation between different countries for the exchange of information on the art, science, and technology of glass by (i) serving as an international center for information exchange, (ii) assisting*

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F. Nicoletti, Stevanato Group, Piombino Dese (PD), Italy

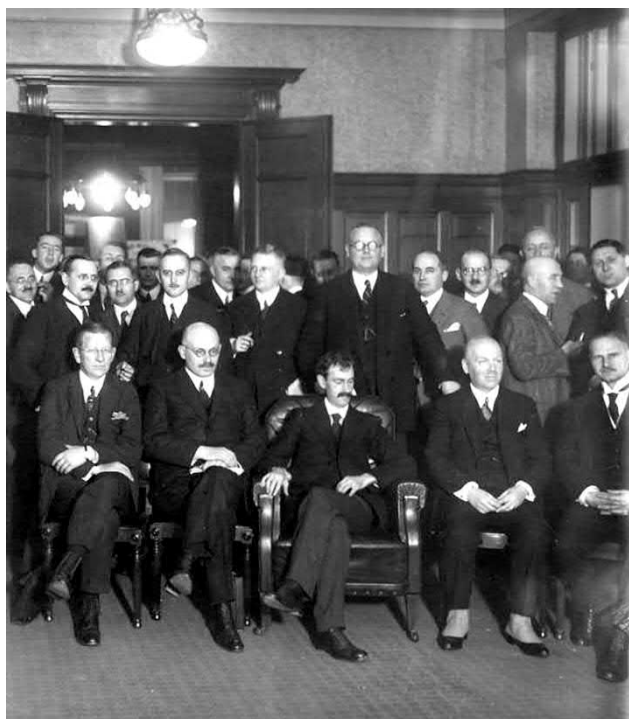


Figure 1 The formal atmosphere of a meeting of glass scientist in 1928 in Aachen. Front row, from left to right: G. R. Gehlhoff, K. Quasebart, W. E. S. Turner, and M. Von Vopelius. H. Maurach standing up behind Turner and Von Vopelius.

everywhere in the development of an interest in glass, (iii) arranging for the holding periodically of International Congresses and Technical Sessions on Glass, and (iv) preparing and issuing reports and surveys having an international character. The task of achieving this was delegated to an Executive Committee.

Managing these goals proved less than straightforward and required significant determination. In 1958 the Executive Committee added a Committee A – later the Coordinating Technical Committee (CTC) – and a Committee B. More changes in 1962–1963 redefined the organization and its working methods, particularly the roles of the Council, with ultimate overall responsibility; the Executive Committee, responsible for technical and scientific matters; and the Bureau, concerned with day-to-day matters.

In 1968 Charleroi, Belgium became the official seat of ICG, under a law giving legal status to international organizations established there. Consequently until 2001 most Treasurers were Belgian. From 1974 the Executive Committee became the Steering Committee (SC), responsible for evaluating, assessing, and approving ICG's activities, and the category of "Associated Members" was introduced. Such constitutional changes required approval by the Belgian authorities, who imposed additional modifications in 1978 and 1999 concerning for

instance the distribution of funds in the event of ICG's dissolution.

In 2001 ICG's base moved to Spain, a change only finally ratified in Belgium in 2005. Funds were transferred to accounts in Spain and Prof. A. Duran became the new Treasurer.

In 2008 a new constitution was approved, embodying changes designed to improve efficiency. The Bureau became the Management Board (MB), and the CTC Chair became its fifth member. Additional ICG membership categories were created: "Associated Member Companies" and "Individual Members." New operating guidelines were written.

Now the Council, consisting of the representatives of the National Participating Organizations (NPOs) and of the Associated Organizations, elects the administration. At its pinnacle is the MB, responsible for the day-to-day running (President, Vice-President, Executive Secretary, Treasurer, and CTC Chair). They are assisted by the SC, i.e. the MB plus up to six members elected by Council including the immediate Past President. Typically they meet twice a year, occasionally three times. Finally the CTC, responsible for all ICG's technical and scientific activities, reports to the SC.

Recently an Advisory Committee (AC) with four representatives from different parts of the world has been formed to work on nontechnical topics of concern to the ICG such as to connect it with other relevant bodies within the glass community. The AC includes members drawn from the SC. Its role and responsibilities are currently under review.

2.2 Personnel

The constitution limits the tenure of officers. The Presidential term has been three years for all but the early years of ICG's history. The Vice-President normally becomes the President elect after two years and accedes as President one year later, ensuring continuity. This natural progression has been broken only rarely, first in the early days of ICG and again in 1995–1996 when F. Nicoletti served temporarily as Vice-President after G. Nightingale resigned prematurely. A significant recent change has been to make the Vice-Presidential selection procedures more transparent. Proposals are submitted by the NPOs and each candidate presents his/her case. The MB and SC vote anonymously, and their choice requires final approval by Council. All ICG presidents are listed in Table 1.

Three people at the end of their terms were elected by Council as Honorary Presidents (Table 2), and six more people active within ICG received Honorary Vice-President status (Table 3). The Executive Secretaries and Treasurers are appointed annually but with no time limit (Table 4).

Table 1 ICG Presidents with their country of origin and dates in service.

W. E. S. Turner	GB	1933–1953
B. P. Dudding	GB	1953–1959
H. R. Lillie ^a	USA	1959–1961
N. von Bülow	D	1961–1961
O. Burch	USA	1961–1962
A. Dietzel	D	1962–1963
B. Long	F	1963–1966
J. M. Stevels	NL	1966–1969
N. J. Kreidl	USA	1969–1972
R. W. Douglas	GB	1972–1975
J. Stanek	CS	1975–1978
P. Gilard	B	1978–1981
H. Scholze	D	1981–1984
V. Gottardi ^a	I	1984–1985
W. R. Prindle	USA	1985–1988
J. P. Causse	F	1988–1991
J. Petzold	D	1991–1994
N. Soga	J	1994–1997
L. D. Pye	USA	1997–2000
H. A. Schaeffer	D	2000–2003
A. Yaraman	TK	2003–2006
H. Arribart	F	2006–2009
F. Nicoletti	I	2009–2012
P. Shou	PROC	2012–2015
M. Choudhary	USA	2015–2018
A. Duran	SP	2018–2021

^a Died prematurely in office.

Table 2 Honorary Presidents.

W. E. S. Turner	GB	1953 (+1963)
B. Long	F	1966 (+1983)
F. Nicoletti	I	2011

Table 3 Honorary Vice-Presidents.

H. Maurach	D	1950 (+1956)
J.C. Hostetter	USA	1950 (+1962)
B.P. Dudding	GB	1959 (+1968)
J.A. de Artigas	E	1965 (+1977)
R. Günther	D	1972
P. Gilard	B	1983 (+2001)

2.3 Funding and Expenditure

The ICG has no permanent office or paid staff although some of the MB receive an honorarium in lieu of expenses. It relies on individuals to give freely of their time and effort. Consequently its running costs are modest. They are financed by subscriptions from NPOs set according to the annual glass output of the respective countries. Additional income arises from Associated Organizations and Member Companies, the sale of publications and analytical standards, and royalties.

Technical Committees can be supported, for instance, through travel expenses for committee members in particular need or funding for projects such as the publication of books and workshop organization.

A major boost in 2005 was the award of an EU grant worth 1.6 million Euros to support specific TC activity (the European Forum on New Glass Applications [EFONGA]). Outcomes include the ICG Roadmapping process, the Montpellier Summer School, and an enhanced TC structure.

2.4 Web Pages

The official ICG web site is at www.icglass.org. Initially hosted by the University of Sheffield, it was transferred in 2011 to a company offering more facilities. The layout was improved to standards then current, and a Content Managed System was installed, which allowed online updating by anyone with password access, with the intention of offering TCs a platform to advertise their results. A further update in 2015 offers the latest editing facilities including links to social media.

Much of the technical content mirrors that in the annual reports produced by the CTC. Approximately 20 news items are added a year, more than half from NPOs. The number of hits has risen steadily at a rate faster than the overall increase in Internet traffic to almost 0.2 million p.a. in 2015. Web statistics also provide valuable insights into the nature of this traffic, for instance, showing that interest from countries not in ICG is significant. Behind the system is a secure address book. The site also offers TCs file storage facilities with access granted solely to committee members.

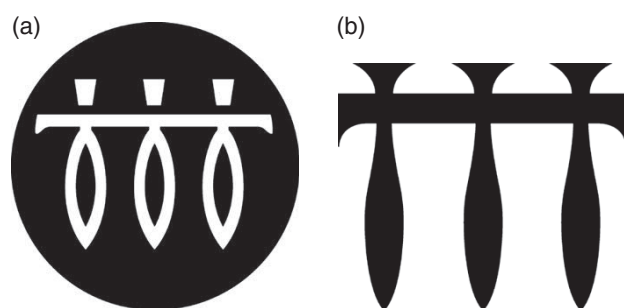
2.5 The ICG Brand

The ICG's formal title, approved in 1994, is "The International Commission on Glass," subtitled "Society of Scientific and Technical Organisations." The word "Society" replaced "Union," used from 1967 to 1994.

In 1967 ICG adopted an Egyptian hieroglyph with the connotation of "brilliance" as its symbol in communications after it had been used first at the 1965 Congress

Table 4 Executive Secretaries and Treasurers of ICG, their nationalities, and dates.

Executive secretaries			Treasurers		
H. Maurach	D	1933–1950	W. Hampton	GB	1950–1953
B.P. Dudding	GB	1950–1953	G. Henry	B	1953–1959
H. Vandecapelle	B	1953–1958	P. Mayaux	B	1959–1961
P. Gilard	B	1958–1961	P. Gilard	B	1961–1975
R. Günther	D	1961–1968	P. Le Clerc	F	1975–1982
C. Thorpe	GB	1968–1975	M. Verburgh	B	1982–1984
H. Rawson	GB	1975–1977	F. Hubert	B	1984–1988
J. Götz	CS	1977–1989	P. van de Putte	B	1988–1997
F. Nicoletti	I	1989–2005	J.P. Delande	B	1997–2001
B. Scalet	I	2005–2008	A. Duran	E	2002–2015
P. Simurka	SK	2008–	M. Pascual	E	2015–

**Figure 2** The 1967 (a) and 1994 (b) ICG logos.**Figure 3** The 2010 ICG symbol.

(Figure 2). A simpler version was designed in 1994. Over time unapproved modifications appeared, and so it was redesigned in 2010 by ABIVIDRO in a contemporary style with strict guidelines for its use (Figure 3). Blue is the official ICG color, chosen in 1999.

3 The ICG Committees

3.1 The Coordinating Technical Committee and Its Technical Committees

From its inception, the ICG appreciated the value of working on technical issues together, and still today it

depends on its Technical Committees (TCs). A program was first formulated and agreed in 1950. Seven areas were identified: definitions, furnace efficiency survey methodology, effects of iron, annealing, international specifications, chemical and physical testing, and publication lists. Not until 1957 was a working framework devised though, based on a Committee A, “Science and Technology,” and a Committee B, “Form, Design, and Decoration.”

Subsequently Committee B struggled to formulate a working plan. It had no natural constituency within the ICG and many with interests in art, archeology, and history belonged to other global organizations (e.g. the International Association of the History of Glass). Finally a TC on “Archaeometry of Glass” was created in 1984 to bring artists and historians into the ICG and was ably led by Dr. R. Brill for many years.

Meanwhile Committee A elected a chair, secretary, and four members. Five subcommittees (SC A1–A5) were tasked to work on Definitions and Terminology, Chemical Durability, Temperature-Viscosity relations, and Furnace Operation. Increasing activity required better communications: conferences, publications, and annual reports. The SC A6 on “Mechanical Properties” was formed in 1961, and five more SCs were created in 1964.

In 1971 a fundamental overhaul clarified operating procedures and introduced more effective progress evaluation. TC Chairs were allowed longer in office, 3 + 3 + 3 years, with the possibility of reelection after one year, to promote continuity. Committee A became the CTC in 1983.

The CTC supervises and coordinates the activities of the various TCs, which carry out applied scientific investigations. Operating procedures continue to be reviewed and revised. The CTC Chair is appointed for 3 + 2 + 2 years, its Vice Chair is appointed for 3 + 2 years, and

Table 5 CTC Chairs (Committee A before 1983).

1957–1965	J. M. Stevels	NL
1965–1972	E. Plumet	B
1972–1977	H. Scholze	D
1977–1982	G. P. Smith	USA
1982–1987	H. Rawson	GB
1987–1992	H. A. Schaeffer	D
1992–1997	A. Yaraman	TK
1997–2004	H. de Waal	NL
2004–2009	K. Bange	D
2009–2016	R. Vacher	F
2016–	H. Inoue	JP
CTC Secretaries		
1961–1966	P. Migeotte	(B)
1966–1972	H. Guillaume	(B)
1983–1988	R. Fidoten	(USA)
1988–1996	P. Sewell	(GB)
1996–	J. M. Parker	(GB)

the Secretary is reappointed annually (see Table 5). Additionally five members are appointed for 3 + 2 years. Meetings are either technical or business. TC Chairs can attend both but are specifically invited to the annual CTC technical meeting.

Over 500 experts are TC members, selected roughly equally from universities, research institutions, and industry. Their access to resources is contributed freely in the pursuit of the objectives of the individual TCs. They gain from sharing knowledge and expertise. Formally, for an individual to join an ICG committee requires the approval of the NPO responsible for that individual's country of domicile and ICG Council. Committee chairs though often approach suitable individuals initially and vice versa.

Technical Committees undertake laboratory round robins, comparative studies, topical meetings, and compile information (e.g. publishing scientific and technical papers and reports and assisting in creating standards and books). They also disseminate knowledge on glass in advanced educational courses and workshops. TCs communicate regularly and meet at least once annually, often at ICG meetings.

From 2009 TCs have been organized into clusters (basics; characterization; applications; glass production; communication, education, and history), each supported by a CTC member. Cooperation across cluster boundaries is encouraged as appropriate. The CTC publishes an annual report and evaluates TC activity.

Over the years many TCs have blossomed, fulfilled their roles, and closed. Others have evolved as circumstances changed. Some are new or even reformed. These changes

are driven by new inventions, new legislation, and different ways of communicating in the glass community. A summary is given in Table 6. A full history is in [2].

3.2 Membership

ICG's members are primarily national societies representing glass technologists and scientists in their country. These NPOs each appoint two representatives onto its governing body, the ICG Council. Where no National Glass Society exists, an appropriate business, university, or research institute can be assigned the status of NPO. Applications in the first place are made to the Executive Secretary.

Membership is dynamic. The initial group of six NPOs in 1933 is now 33. The countries currently represented on ICG Council are listed in Table 7a and b (2015) together with the dates they first joined. A few countries are no longer represented (Australia, Egypt, Indonesia, Ireland, Philippines, Yugoslavia), some have been represented by different NPOs at different points in their history, some NPOs have adopted new titles, and international borders have not remained the same. More details are in [2].

Six bodies either with international glass interests or more focused local interests have been granted the role of Associated Organization. Constitutional changes in 2008 allowed national and multinational companies with a strong glass bias to become Associated Member Companies. This stimulates involvement in TCs and other activities. As of 2015 there are 16 such members.

Exceptionally, Individual Members can be appointed.

4 Public Activities

4.1 Congresses and Conferences

ICG Congresses and Conferences provide valuable opportunities for glass scientists and technologists to meet and share information (Table 8). The first were in Venice, Italy, and the United Kingdom (London/Sheffield). Dr. Maurach had hoped to organize a third in Berlin in 1939 but WWII intervened. The next was not until 1953. Since then they have been triennial.

An appendix to the constitution gives rules for running International Congresses on Glass. While the primary organizers are the NPOs in the destination country, key ICG officers join an International Advisory Committee and a Scientific Committee, providing support and ensuring continuity. The Congress host is approved six years in advance by the ICG Council, following an invitation to all NPOs to bid.

Table 6 Technical Committees: title (years of operation).

TC01	Terminology (1958–1982) Publication and Terminology (1983–1994) Information and Communication (1996 to present)
TC02	Chemical Durability and Analysis (1958 to present)
TC03	Quality of Glass (1958–1975) Basic Glass Science (2001–2014) Structure and Properties (2014 to present)
TC04	Temperature-Viscosity Relations (1958–1970) Glasses for Medicine and Biotechnology (2003 to present)
TC05	Furnace Operation (1958–1978) Nuclear and Hazardous Waste Vitrification (2006 to present)
TC06	Mechanical Properties of Glass (1961–2015) Glass Strength (2015 to present)
TC07	Devitrification (1964–1995) Nucleation, Crystallisation and Glass Ceramics (1995 to present)
TC08	Reference Glasses (1964–1985) Glass Transition (2008–2015)
Tc09	Electrical Properties (1964–1980) Nanomechanics (2008–2011) Energy Efficiency for Glass Production (2013 to present)
TC10	Optical Properties of Glass (1964 to present)
TC11	Contact between Glass and Refractories (1964–2008) Materials for Glass Manufacturing (2008–2016) Refractory Materials (2017 to present)
TC12	Documentation (1967–1994) Glass, Society and Environment (2008) Pharma Packaging (2012 to present)
TC13	Environment (1973 to present)
TC14	Gases in Glass (1978 to present)
TC15	Instrumentation, Measurement and Automation (1982–2000) Sensors and Advanced Control (2000–2013)
TC16	Sol–Gel Glasses (1983–2007) Nanostructured glass (2007 to present)
TC17	Archaeometry of Glass (1984 to present)
TC18	Properties of Glass-Forming Melts (1986–2011) Glass Melting Technology (2011 to present)
TC19	Physical Methods for Studying Glass Surfaces (1986–2000) Glass Surface Diagnostics (2000–2013) Surface Properties (2017 to present)
TC20	Glasses for Optoelectronics (1989 to present)

Table 6 (Continued)

TC21	Modelling of Glass Melts (1990–2000) Modelling of Glass Melting Processes (2000–2013) Glass Furnace Design and Operation (2013 to present)
TC22	Electrochemical Behaviour of Glass Melts (1992–2006) Structure–property relations (2009–2013)
TC23	Education and Training in Glass Science and Engineering (1992 to present)
TC24	Coatings on Glass (1995 to present)
TC25	Modelling of Glass Forming Processes (2000–2017)
TC26	Biosolubility of Glass (2000–2005) Structure and Vibrations (2009 to present)
TC27	Atomistic Simulation (2009 to present)
TC28	Glass Fibres for Reinforcement and Insulation (2017 to present)

Early congresses were multilingual with simultaneous translation. Now they are in English. Most offer publication. In 1998 for the first time papers were published on CD ROM. A more complete version of the table below gives Conference Presidents, Conference Organizers, and references to the published proceedings [2]. Two important papers have analyzed the evolution of the Congresses and submission trends such as the proportions of papers from industry vs. academia [2, 3].

ICG Congresses have grown significantly to between 700 and 1000 attendees who deliver up to 900 papers and posters. Their special features include:

- 1) Invited lectures reviewing progress in traditional areas and in new subjects such as optics, photonics, electronics, nanotechnology, coating technology, and biotechnology.
- 2) Sessions organized by TCs on their work.

When there is no Congress, Annual Conferences are held. These attract 200–400 participants and are an important part of the ICG calendar [2]. The Council, SC, and CTC meet there.

4.2 Summer and Winter Schools

Technical Committee 23 is specifically tasked with supporting the education of young glass technologists. Over many years short course teaching has been undertaken throughout the world using expertise available within ICG. This approach crystallized during the EFONGA project (2005–2009) in the initiation of an Annual Summer School based at a single site (Montpellier, France). It uses a core group of lecturers with new teachers recruited annually to give each school a distinctive flavor.

Table 7a Member countries in the order they first joined and current representative NPO.

France	1933	Institut du Verre (IV)
Germany	1933	Deutsche Glastechnische Gesellschaft (DGG)
Italy	1933	Stazione Sperimentale del Vetro (SSV)
Spain	1933	Sociedad Espanola de Ceramica y Vidrio (SECV)
United Kingdom	1933	Society of Glass Technology (SGT)
USA	1933	American Ceramic Society (ACS)
Belgium	1936	INISMa-InV
Czech Republic	1936	Czech Glass Society (CGS)
Denmark	1936	Danish Ceramic Society
Japan	1936	Ceramic Society of Japan (CSJ)
India	1948	Central Glass and Ceramic Research Institute
Netherlands	1948	Nationaal Comité van de Nederlandse Glasindustrie (NCNG)
Sweden	1948	GLAFO – the Glass Research Institute
Poland	1958	Institute of Glass and Ceramics, IGC, Cracow Branch
Brazil	1963	Associacao Technica Brasileira das Industrias Automaticas de Vidro (ABIVIDRO)
Canada	1965	Université LAVAL, Centre d'optique, photonique et laser
Hungary	1971	Szilikatipari Tudományos Egyesület
Russia	1979	National Commission on Glass, NCG, of the Russian Academy of Sciences
Turkey	1981	Türkiye Sise ve Cam Fabrikalari A.S.
China	1982	Chinese Ceramic Society (CCS)
Greece	1984	Hellenikos Hyalourgikos Syndesmos
Argentina	1988	Instituto Nacional de Tecnologia Minera (INTEMIN)
Bulgaria	1992	Institute of Physical Chemistry, Sofia
Mexico	1992	Vitro Vidrio y Cristal, S.A.
Romania	1992	University Polytechnic of Bucharest
Korea	1993	Korean Ceramic Society
Liechtenstein	1993	Ivoclar AG
Thailand	1996	Bureau of Community Technology, Ministry of Science and Technology
Portugal	1998	Centro de Quimica Estrutural Instituto Superior Tecnico, Lisbon
Slovakia	1999	Slovak Glass Society (SGS)
Finland	2003	Glaston Finland Oy
Serbia	2008	University of Novi Sad Faculty of Technical Sciences, Novi Sad
Iran	2015	Iran Glass Association

The following countries have also been represented at some time during the period 1933–2018: Australia (1966–1977; 2008–2014), Egypt (1957–2003), Greece (1984–2017), Indonesia (1981–2003), Ireland (2002–2005), Philippines (1998–2009), Serbia (2008–2015), and Yugoslavia (1970–1992).

The school has evolved as its teachers have learned how best to develop understanding and stimulate a deep interest in the subject. Key aspects are the group project work undertaken competitively during the week and small group tutorials that supplement the 20 lectures. Participants and teachers are encouraged to network, something that can continue into their professional lives, and to question everything. This school is in its 11th year (2019); a major textbook entitled *Teaching Glass Better*

covering both the historical development and central themes of the school was published to celebrate the 10th anniversary in 2018.

Following enthusiasm for extending the schools beyond Europe, a Winter School was run in Shenzhen, China, in 2014 to encourage wider participation from Far Eastern countries. Teaching, by lecturers from the Montpellier School and the local community in China, was in English. The second school ran in Wuhan in

Table 7b Member countries in alphabetical order, date they first joined) and current representative NPO.

Argentina	1988	Instituto Nacional de Tecnologia Minera (INTEMIN)
Belgium	1936	Institut du Verre, Federation des Chambres Syndicales de l'Industrie du Verre
Brazil	1963	Associacao Technica Brasileira das Industrias Automaticas de Vidro (ABIVIDRO)
Bulgaria	1992	Bulgarian Commission on Glass
Canada	1965	Université LAVAL, Centre d'optique, photonique et laser
China	1982	Chinese Ceramic Society (CCS)
Czech Republic	1936	Czech Glass Society (CGS)
Denmark	1936	Danish Ceramic Society
Finland	2003	Glaston Finland Oy
France	1933	Institut du Verre (IV)
Germany	1933	Deutsche Glastechnische Gesellschaft (DGG)
Hungary	1971	Szilikatipari Tudomanyos Egyesulet
India	1948	Central Glass and Ceramic Research Institute
Iran	2015	Iran Glass Association
Italy	1933	Stazione Sperimentale del Vetro (SSV)
Japan	1936	Ceramic Society of Japan (CSJ)
Korea	1993	Korean Ceramic Society
Liechtenstein	1993	Ivoclar AG
Mexico	1992	Vitro Vidrio y Cristal, S.A.
Netherlands	1960	Nationaal Comite van de Nederlandse Glasindustrie (NCNG)
Poland	1958	Institute of Glass and Ceramics, IGC, Cracow Branch
Portugal	1998	ICEMS
Romania	1992	University Polytechnic of Bucharest
Russia	1979	National Commission on Glass, NCG, of the Russian Academy of Sciences
Slovakia	1999	Slovak Glass Society (SGS)
Spain	1955	Sociedad Espanola de Ceramica y Vidrio (SECV)
Sweden	1948	GLAFO – the Glass Research Institute
Thailand	1996	Bureau of Community Technology, Ministry of Science and Technology
Turkey	1981	Turkiye Sise ve Cam Fabrikalari A.S.
United Kingdom	1933	Society of Glass Technology (SGT)
USA	1933	American Ceramic Society (ACS)

The following countries have also been represented at some time during the period 1933–2018: Australia (1966–1977; 2008–2014), Egypt (1957–2003), Greece (1984–2017), Indonesia (1981–2003), Ireland (2002–2005), Philippines (1998–2009), Serbia (2008–2015), and Yugoslavia (1970–1992).

2016 just before ICG's Shanghai Congress. Subsequent schools have adopted the same venue and the fifth will run in 2019. Generous grants from the Chinese allowed exchange of students between the Montpellier and Wuhan schools in 2018, creating a new and much appreciated dimension to this exercise. Other venues around the world are being considered, and a school focused on optical properties is planned in North America (Laval, Canada) immediately after the 2019 ICG Congress. An unexpected bonus has been the sharing of different teaching styles among the staff.

4.3 Publications

From 1957 the ICG has actively supported publication of bibliographies, reviews, or books with an international flavor. It has always had committees tasked with this role. ICG books in print are housed at the DGG offices in Germany and can be purchased by direct application. They are listed on the ICG web site: www.icglass.org. Of the 50 or so books supported to date, 12 have been multilingual dictionaries, 6 cover chemical analysis/durability measurement methodologies, and another 6 cover

Table 8 ICG Congress record.

	Venue	Year	Participants	Countries	Papers	Posters
I	Venice	1933	200	8	42	
II	London-Sheffield	1936	552	20	72	
III	Venice	1953	244	19	59	
IV	Paris	1956	555	23	62	
V	München	1959	755	30	62	
VI	Washington	1962	716	24	119	
VII	Brussels	1965	848	26	172	
VIII	London	1968	720	29	250	
IX	Versailles	1971	730	28	92	
X	Kyoto	1974	813	27	153	
XI	Prague	1977	1176	32	263	
XII	Albuquerque	1980	685	30	159	
XIII	Hamburg	1983	890	34	199	100
XIV	New Delhi	1986	650	29	177	87
XV	Leningrad	1989	2017	35	561	
XVI	Madrid	1992	644	40	185	300
XVII	Beijing	1995	660	35	225	228
XVIII	San Francisco	1998	925	48	300	500
XIX	Edinburgh	2001	730	41	443	216
XX	Kyoto	2004	902	47	339	178
XXI	Strasbourg	2007	827	48	311	360
XXII	Salvador	2010		30	380	With posters
XXIII	Prague	2013	703	43	338	142
XXIV	Shanghai	2016	803	34		

Table 9 Weyl Awardees.

1977	Prague	Peter Schultz	USA
1980	Albuquerque	Denis Ravaine	France
1983	Hamburg	Bruno Smets	Netherlands
1986	New Delhi	George Scherrer	USA
1989	Leningrad	Terry Michalske	USA
1992	Madrid	Yuichi Watanabe	Japan
1995	Beijing	Edward Pope	USA
1998	San Francisco	Sabyasachi Sen	India
2001	Edinburgh	H. Ebendorff-Heidepriem	Germany
2004	Kyoto	M. Dejnek	USA
2007	Strasbourg	A. Hayashi	Japan
2010	Salvador	J. Mauro	USA
2013	Prague	L. Wondraczek	Germany
2016	Shanghai	Qiang Fu	USA

physical properties. Besides, five have been concerned with furnace technology (sensors, regenerators, refractories), two with electrical properties, and two list educational establishments. Two have been histories of ICG. Others have reviewed optoelectronics, biomaterials, crystallization and glass ceramics, electrochemistry, and bubble formation. Books written by members of TC04 (biomaterials), TC17 (history of glass bead making in India), and TC20 (optical properties) are among those recently supported. Finally, three recent texts form a series on “Making Glass Better” and record road-mapping exercises (2010, 2014, 2015); “Teaching Glass Better” (2018) is the most recent addition and has initiated a new direction.

Finally, an attempt in 1950 to produce an ICG journal foundered because its remit overlapped with journals already published by its NPOs.

4.4 Prizes Awarded

One way in which ICG supports the global glass community, particularly its younger members, is to encourage and support excellence by offering prizes. The Woldemar A. Weyl International Glass Science Award was established in 1976 by the Pennsylvania State University and ICG. It honors Prof. Weyl (1901–1975) who was well known internationally as an imaginative and innovative scholar and teacher. Professor Weyl wished to give his young associates every opportunity to participate in scientific meetings. Therefore, the Award recognizes outstanding, innovative, young glass scientists, preferably not over 35 years old, by funding a lecture to be given at each ICG Congress. Anyone can submit nominations to the Chair of the Glass and Optical Materials Division of the American Ceramic Society (see Table 9).

The ICG Prize in Memory of Prof. Vittorio Gottardi was instituted in 1986. It celebrates Prof. Gottardi (+1985), ICG President from 1984 to his death, in October 1985, and recognizes meritorious research, development, teaching, writing, management, or commercial achievements in the field of glass. The spectrum of activities qualifying for recognition is purposely broad so that workers throughout the glass community are eligible. The Prize is presented annually to a person not past their 39th birthday when nominated and not past their 40th at the date of the award. Nominations are submitted by NPOs (Table 10).

To recognize outstanding lifetime contributions to the international glass community, the ICG established the ICG President’s Award in 1994, in part to honor its first president, Prof. Turner. Council members nominate deserving individuals (Table 11).

Inaugurated in 2002, the Turner Award recognizes those who have made a noteworthy contribution to ICG’s

Table 10 Gottardi Prize winners.

1987	P. Fournier (F) and F. Geotti-Bianchini (I)
1988	A. Durán Carrera (E)
1989	H.J. Barklage-Hilgefort (D)
1990	K. Hirao (J)
1991	D.M. Krol (NL)
1992	M. Guglielmi (I)
1993	E.D. Zanutto (BZ)
1994	R.G.C. Beerkens (NL)
1995	M. Tatsumisago (J)
1996	R.K. Brow (USA)
1997	M. Mennig (D)
1998	X. Zhao (PROC)
1999	K. Nakanishi (J)
2000	A.G. Clare (USA)
2001	T. Uchino (J)
2002	J. Deubener (D)
2003	M. Mika (CZ)
2004	B. Hehlen (F)
2005	S. Jiang (CN)
2006	K. Tadanaga (J)
2007	L. Cormier (F)
2008	K. Fujita (J)
2009	R. Keding (D)
2010	M Pascual (E)
2011	J. Mauro (USA)
2012	T. Honma (JP)
2013	L. Wondraczek (D)
2014	J. Jones (UK)
2015	D. Brauer (D)
2016	R. Martin (UK)
2017	A. Goel (USA)
2018	S. Zhou (CN)

TCs. The CTC selects the awardees (Table 12), and the presentation is made at an Annual ICG meeting or Congress.

5 Perspectives

Dramatic changes in society require that ICG “moves with the times.” Already the Globalization of Industry has blurred the boundaries of the domains of activity of NPOs. So the trend to populate new membership categories will continue and influence ICG. Countries with

Table 11 President's Award winners.

1995	A. R. Cooper	N. J. Kreidl	J. Stanek	
1998	M. Cable	J. Petzoldt	H. Rawson	
2001	G. Fuxi	P. Gilard	O. Mazurin	
2004	C. Guillemet	F. Nicoletti	N. Soga	
2007	J. Barton	A. Varshneya	A. Yaraman	
2010	G. Frischat	D. Pye	H. Schaeffer	
2013	J. Matousek	I. Gutzow	S. Sakka	D. Day
2016	N. F. Borelli	A. Makashima	J. M. Parker	Peng Shou

Table 12 Turner Award winners.

2002	O. Çorumluoğlu (TK)
2003	P. Polato (I)
2004	R.M. Brill (USA) and J.M. Parker (UK)
2005	H. de Waal (NL)
2006	U. Kircher (D) and I. Smith (UK)
2007	E. Guadagnino (I)
2008	R. Beerkens (NL)
2009	W. Höland (LI)
2010	K. Bange (D)
2011	R. Conradt (D)
2012	S. Tanabe (J)
2013	G. Albayrak (TK) and C. Anderson (F)
2014	B. Scalet (I)
2015	D. Köpsel (D) and V. Rupertus (D)
2016	A. Boccaccini (D) and S. Slade (UK)
2017	R. Vacher (F)
2018	J. Marra (USA)

little or no representation must be encouraged to participate.

ICG is an ideal platform for industry–academia collaboration and for interdisciplinary projects, as EFONGA showed. Conversely both industrial and academic workers are under growing time pressures and tighter financial constraints. TCs are meeting less often and progressing more slowly. ICG needs to demonstrate the added value

of involvement to TC members, and their employers in industry and academia, by publishing exciting research in high impact journals, generating excellent texts (road-maps, standards) and working on international issues such as energy efficiency, sustainability, and environmental protection. Ways of financing increased activity and enhancing communications are being investigated via an internal exercise called Project 2030.

ICG already offers educational support to the next generation of workers, but this needs extending. Involving younger participants in TCs can support their development and enliven TC activities. The recent creation of a Young Person's Committee has already led to the introduction of Mentoring Events at the most recent ICG Annual Conferences (2017, 2018) and further developments are planned.

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Section X. History



This section devoted to a broad history of glass cannot begin without a mention of Pliny's legendary account of Phoenician merchants who observed a melting reaction between the natron blocks they took to support their cauldron and the sand of the beach where they set a fire to prepare their meal ([1]; Appendix X.A). Glass was in fact nearly 2000 years old at Pliny's time. As wittily noted by the eminent glassmaker Georges Bontemps (1799–1883), if not entirely legendary the story would rather have been that of traders en route to deliver their cargo to some local soda-lime silica glass factory [2]!

More informative in Pliny's descriptions are the technical skills displayed by ancient glassmakers who could fetch very high prices for outstanding glass items and who were in addition able to distinguish fake from real gems by a lower density, a lower thermal conductivity (in modern parlance), or the presence of bubbles and other defects. And Pliny also left interesting reflections on the dual creative and destructive effects of fire, on obsidians (opsian), on the reputation of Egyptian soda, as well as doubts concerning the veracity of Petronius' famous account of flexible glass in the *Satyricon*.

In Eurasia, glass has been exchanged over long distances for 2 million years in the form of obsidian whose unique sharpness made it a highly valued commodity. Obsidians are not so common volcanic rocks. Nowadays, what make them specially important is that their trace-element compositions constitute a fingerprint of their geographical origin, which may have been hundreds or even thousands of km from the sites where obsidian artifacts are now found. In the first chapter, R. Tykot describes how prehistoric trade patterns in western Mediterranean, Near East, and Latin America can be reconstructed from trace-element analyses of obsidians,

which can nowadays be made on the spot, thanks to modern X-ray fluorescence instrumentation; also summarized is the information that can be drawn on ancient cultures from studies of the wear or weathering of the artifacts themselves (Chapter 10.1).

For a very long time, glass had been a familiar material when glassmaking was invented less than four millennia ago in the Near East and Egypt. Although its origins remain clouded in mystery, they were likely related to ceramic or metallurgical activities. These resulted in a diversity of chemical compositions that is well documented throughout time and space by the thousands of analyses now available [3, 4]. In any case, the beginnings of glassmaking attests to the long and tenacious efforts driven by the sheer curiosity of artisans who were obviously unable to guess the nature of the products that would be the long-term outcome of their work. Clearly, aesthetic interest was first raised by the vivid colors and gem-like aspect of glass. It gave rise to the variety of coloration methods reviewed by A. Shortland and P. Degryse who also describe how chemical and isotopic analyses of ancient artifacts can yield reliable information on the provenance of the raw materials used, production processes, and places of production (Chapter 10.2).

At the turn of the millenia, of particular importance were the inventions of glass blowing and of transparent glass made from quartz sand and naturally pure sodium carbonate salts called *natron*. Glass production then became a real industry with the establishment of the first-ever world market whereby, thanks to clear competitive advantages, large amounts of glass produced mostly in the Levant were exported throughout the Mediterranean area and beyond either as ingots (Figure 2) or finished products. The various facets of this activity are

Figure 1 Through 25 centuries of glassmaking, an art travel at the Glasmuseum Hentrich of Dusseldorf. *Source:* Photos Studio Fuis, courtesy Dedo von Kerssenbrock-Krossigk. (a) Bowl, Achaemenid Empire, Persia, late fifth/early fourth century BCE (P 1973–12). Colorless glass with a slight green tinge, mould-melted, ground. D. 16 cm; (b) Vase “Les feuilles des douleurs passées,” Emile Gallé, Nancy, 1900 (P 1970–13). Opaque-brown glass, partial blue overlay with silver foil, colorless overlay, mould-blown. H. 14.3 cm. Gift of Helmut Hentrich; (c) Bowl, reputedly found in Mainz, first half of the fourteenth century (P 1985–297). Colorless glass, free-blown, applied blue threads. D. 25.6 cm; (d) Bowl, Middle East, Sassanid Empire, fifth or sixth century CE (P 1966–4). Colorless glass, blown, cut. H. 7.5 cm. Gift of Helmut Hentrich; (e) Brush-holder vase (“Vase porte-pinceaux”), designed by Emile Gallé, Nancy, made by Burgun, Schverer & Co., Meisenthal, France, 1884 (LP 2006–392). Colorless glass and melted-on glass powder, free-blown, applied handles, engraved, enameled, and gilded. H. 10.5 cm. Bequest of Gerda Koepff; (f) Titule goblet and Grail bowl from the “Percival” series, J. & L. Lobmeyr, Vienna, design by Richard von Kralik, made by Meyr's Neffe, Winterberg, South Bohemia, 1889 (P 1975–77). Rosaline glass with colorless overlay, mould-blown; gold, and enamel-painted. H. (covered goblet) 68.3 cm; (g) Covered goblet, Maurice Marinot, Bar-sur-Seine, France, 1925 (P 1967–28). Colorless glass with dense-gold-colored bubbles between the layers, free-blown, cut. H. 37 cm. Gift of Florence Marinot; (h) Glass bottle with thread decoration, Eastern Mediterranean, first half of the third century CE (P 1970–3). Colorless and opaque yellow glass, free-blown, applied threads. H. 21.6 cm. Gift of Dr. Günther Henle, Klöckner-AG; (i) Covered beaker with childrens' bacchanal, Potsdam, Brandenburg, Germany, engraved by Gottfried Spiller, Berlin, c. 1700 (P 1940–132). Colorless glass, mould-blown, cut, engraved. H. 26.7 cm; (j) Vase, Erwin Eisch, Frauenau, 1962 (P 199–348). Grayish-blue, red, and yellow glass, mould-blown, deformed, with partial overlay and applications. H. 29.3 cm; (k) Lamp, Johann Loetz Witwe, Klostermühle, south Bohemia, c. 1902; pewter mount probably designed by Franz Pankok (LP 1992–11). Yellow glass, colorless overlay, blown in a ribbed mold, applied threads, iridized; tin, cast, engraved, eight moonstones. H. 58.1 cm. Loan from Freunde des Kunstpalastes; (l) Jutta Cuny, “Narcisse endormi,” Lomazzo near Como, Italy, 1983 (P 1993–24). Optical glass, sandblasted; Sèvres biscuit porcelain. 30 × 72 × 26 cm. Gift of Ruth-Maria Franz; (m) Tall beaker with applied network of threads, Germany, first half of the sixteenth century (LP 1878–44). Yellow-green glass, optically blown, applied blue threads. H. 23.1 cm. Loan from Freunde des Kunstpalastes.

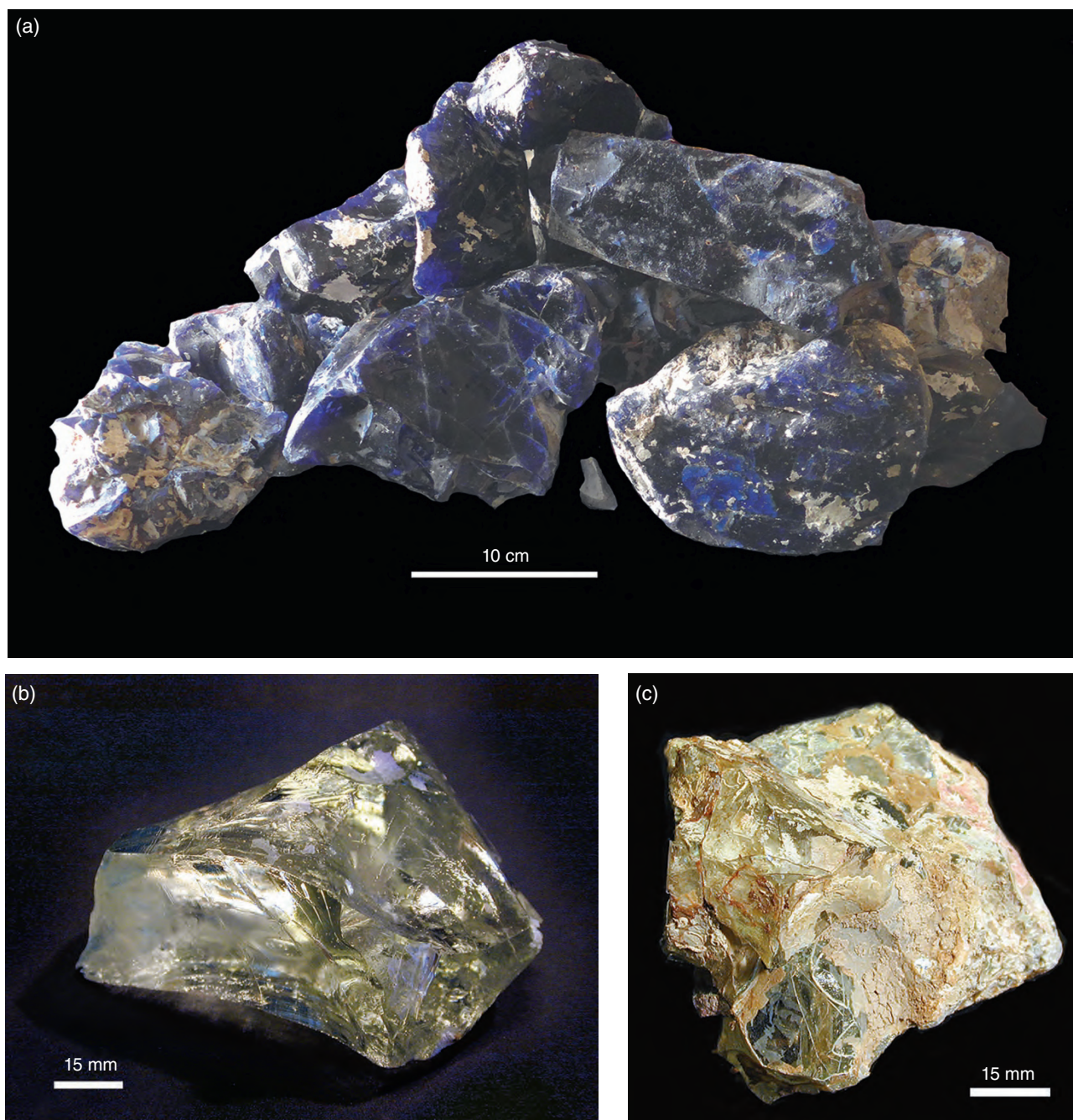


Figure 2 Ingots of Roman glasses similar to those known by Pliny as conserved in ancient Mediterranean shipwrecks. (a) Blue glass from the third century BCE found off Ajaccio, Corsica. Source: Photo Hervé Alfonsi, ARASM; épave *Sanguinaires A* [5]. (b) Fresh and altered Alexandrian glass found in a third century CE shipwreck at Les Embiez, near Cannes [6]. Source: Ingots courtesy D. Foy, photos P. Richet.

addressed by I. Freestone, beginning with melting tanks of up to 20-t capacity and continuing with the chemistry of the glass and its subsequent transparency, coloration, or opacification, its transformation in secondary workshops and the recycling of this valuable resource as cullet (Chapter 10.3).

In Antiquity, glassmaking did not fail to attract the philosophers' interest. Along with the transformation of plain earths into a substance looking like gems, the

kinship of molten glass with metals and the role later played by glass in emerging alchemy were good reasons for pondering over its nature and its place in the philosophy of matter. From early reflections made in Mesopotamia and in Egypt on glasses as molten precious stones, the issue was taken over in Greece. From Empedocles to Plato and Aristotle, the attempts summarized by M. Beretta aimed at explaining the formation of glass in terms of elementary constituents or of *qualities*; they

entertained a close relationship of glass not only with alchemy but also with gem counterfeiting within a theoretical framework that would exert a long-term influence through its transmission to Byzantium (Chapter 10.4).

Of course, these ancient ideas ceased long ago to be relevant to glassmakers. In contrast, the various processes devised in Antiquity for shaping glass have been continuously used since then and are still those of contemporary artists and makers of highly priced crystal-glass items. Before the shaping possibilities offered by the new material were understood, the first forming processes were inspired by ceramic practices. As reviewed by M. Stern, who also pays attention to the social and working contexts of ancient glassmaking, these processes were progressively complemented by casting, pressing, molding, blowing, and hot- and cold-decorative techniques, which could then be combined to shape outstanding items such as gold, cameo, and cage-cup glass pieces; before the invention of the *pontil*, however, blowing did not spread as fast as often assumed because previous processes were already efficient economically (Chapter 10.5).

Coatings, which are an important feature of modern glassmaking, are not a recent invention at all. Under the names of *enamels* (deposited on smooth surfaces) and *glazes* (on porous ones), they were already deposited in Antiquity as thin layers to modify surfaces either for hardening or tightening them or for aesthetic reasons. Like for modern coatings, the most important problems to be solved, described by Ph. Colomban, were (i) to ensure first the wetting of the metal, glass, or ceramic substrate by the precursor powders and, then, a close thermal expansion match between the coating and substrate to avoid either peeling or cracking, and (ii) to find the appropriate agents for coloring or opacifying thin layers; empirically, these problems were solved in a great many different ways throughout the centuries and in various parts of the world as illustrated by the Chinese *celadons*, the Japanese *Raku*, the European porcelains as well as by contemporary production (Chapter 10.6).

In Europe, glassmaking suffered from the fall of the Roman Empire caused by the Barbarian invasions of the fourth and fifth centuries, especially because primary fabrication was lacking. Given that much of antique production is known through finds made in graves or from the Pompei catastrophe, a consequence of the Church prohibition to bury items with the dead is that little is known about European glass production in the early Middle Ages. Whereas written sources document glass production in Venice from the late tenth century, chemical analyses of archeological glass fragments point to a continuous production from Roman times with an important change from natron to plant-ash glasses between the ninth and thirteenth centuries. As documented by M. Verità, the efforts subsequently made to improve composition, for example, by the use of quartz pebble for silica

and carefully washed plant ash for soda, resulted in the invention of the famous clear *cristallo* and of colored specialty products; these made Venice the world leader in glass production from the fifteenth to the seventeenth century and thus prompted imitators to produce their own pieces *à la façon de Venise* (Chapter 10.7).

By far the most extensive body of ancient glass artifacts is exhibited by the stained glass of church windows. Their earliest mentions are found in texts from Late Antiquity. Despite the great many causes of destruction throughout the ages of such a fragile material, extant windows are remarkably abundant in Europe from the thirteenth century. As reported by J.M. Parker and D. Martlew, their religious message could be readily understood in the form of vividly colored images made of flat glass produced by the two already ancient *crown* and *cylinder* processes, whereby glass was first blown to keep a fire polish before being flattened and cut into pieces that are assembled with soft lead *comes*; beginning with *grisaille* and silver staining, other ways to modify the glass color and texture were then developed over the centuries to produce new styles or to restore ancient pieces, sometimes so well that up-to-date analytical means are needed to distinguish original from restored parts (Chapter 10.8).

Glass had to wait until the eighteenth century to recover in European households the importance it had in Roman times. With low production volumes, melting and forming processes basically remained those designed in Antiquity. The first important changes described by M.-H. Chopinet and P. Richet were the substitution of coal for wood as a fuel in England in the early seventeenth century and the invention of the table-casting process for plate glass half a century later in France; but it was only from the beginning of the nineteenth century that the birth of both modern chemistry and thermodynamics triggered a continuous string of improvements to save energy with regenerators, to design more efficient furnaces, to switch from pot to tank melting, to improve chemical composition, and to produce flat, plate, and container glass with the first mechanical processes designed at the beginning of the twentieth century (Chapter 10.9).

That glass has been the science material *par excellence* is then justified by P. Richet who points out its original importance in optics and alchemy and its subsequent key roles in the exploration of the universe with the telescope and the microscope, in the design of thermometers, barometers, and other instruments that were at the roots of the scientific revolution, in chemistry, in the birth of electrical science, and in the research that began with the cathode-ray tube and eventually led to subatomic physics; all of these fields benefited along the way from progressively improved glasses in terms of both homogeneity and composition (Chapter 10.10).

The history of glass science is the next topic dealt with. Like glassmaking processes, conceptions of the nature of

glass changed little from Antiquity to the seventeenth century, tells P. Richet in a story where, given the lack of such an account in the literature, care has been taken to bring to light the work made by numerous workers throughout the ages; although the real beginnings of glass science can be dated to the picture of the glass transition given by Descartes, a distinct glass science relying on concepts specifically designed to account for the special properties of glass-forming liquids appeared only in the early twentieth century when new experimental tools became available to investigate their properties and determine their structures (Chapter 10.11).

Finally, we note that pure art is beyond the scope of the Encyclopedia in spite of a rich tradition that dates back to the very beginnings of glassmaking. The reason is that the original insights on glass *as a material* that can be drawn from studies of past items have been summarized in previous chapters so that a review of ancient or modern masterpieces from an art-history perspective would add little in these scientific and technical respects. Hence, it is better to illustrate the glassmakers' artistry with a selection of items that covers 25 centuries of activity (Figure 1), and to draw the attention of the reader interested to a few standard reference books on these topics [7–12].

It has nonetheless been deemed appropriate to conclude the *Encyclopedia* with a chapter on Glass museums or museums holding significant glass collections. As noted by D. van Kerssenbrock-Krossigk, these collections were first made by the powerful or wealthy of Antiquity who considered glass vessels and sculptures as treasures: these collectors began a tradition that was pursued by princely houses before benefiting from the general expansion of museums in the nineteenth century and, afterward, from the specialization of some in the decorative or regional arts; more recently, interest has in addition been paid not only to conservation and exhibitions, but also to teaching and to technical and scientific investigations of glass collections (Chapter 10.12).

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Appendix X A Pliny's Famous Account of the Origin of Glass in His *Natural History*

LXV. That part of Syria which is known as Phoenicia and borders on Judea contains a swamp called Candebia amid the lower slopes of Mount Carmel. This is supposed to be the source of the River Belus, which after traversing a distance of 5 miles flows into the sea near the colony of Ptolemais. Its current is sluggish and its waters are unwholesome to drink, although they are regarded as holy for ritual purposes. The river is muddy and flows in a deep channel, revealing its sands only when the tide ebbs. For it is not until they have been tossed by the waves and cleansed of impurities that they glisten. Moreover, it is only at that moment, when they are thought to be affected by the sharp, astringent properties of the brine, that they become fit for use. The beach stretches for not more than half a mile, and yet for many centuries the production of glass depended on this area alone. There is a story that once a ship belonging to some traders in natural soda put in here and that they scattered along the shore to prepare a meal. Since, however, no stones suitable for supporting their cauldrons were forthcoming, they rested them on lumps of soda from their cargo. When these became heated and were completely mingled with the sand on the beach, a strange translucent liquid

flowed forth in streams; and this, it is said, was the origin of glass.

LXVI. Next, as was to be expected, Man's inventive skill was no longer content to mix only soda with the sand. He began to introduce the magnet stone also, since there is a belief that it attracts to itself molten glass no less than iron. Similarly, lustrous stones of many kinds came to be burnt with the melt and, then again, shells and quarry sand. Authorities state that in India glass is made also of broken rock-crystal and that for this reason no glass can compare with that of India. To resume, a fire of light, dry wood is used for preparing the melt, to which are added copper and soda, preferably Egyptian soda. Glass, like copper, is smelted in a series of furnaces, and dull black lumps are formed. Molten glass is everywhere so sharp that, before there is the least sensation, it cuts to the bone any part of the body on which it splutters. After being reduced to lumps, the glass is again fused in the workshop and is tinted. Some of it is shaped by blowing, some machined on a lathe, and some chased like silver. Sidon was once famous for its glassworks, since, apart from other achievements, glass mirrors were invented there.

This was the old method of producing glass. Now, however, in Italy too a white sand which forms in the River Volturno is found along 6 miles of the seashore between Cuma and Literno. Wherever it is softest, it is taken to be ground in a mortar or mill. Then it is mixed with three parts of soda, either by weight or by measure, and after being fused is taken in its molten state to other furnaces. There it forms a lump known in Greek as "sand-soda." This is again melted and forms pure glass, and is indeed a lump of clear colorless glass. Nowadays, sand is similarly blended also in the Gallic and Spanish provinces. There is a story that in the reign of Tiberius there was invented a method of blending glass so as to render it flexible. The artist's workshop was completely destroyed for fear that the value of metals such as copper, silver, and gold would otherwise be lowered. Such is the story, which, however, has for a long period been current through frequent repetition rather than authentic. But this is of little consequence, seeing that in Nero's principate there was discovered a technique of glass-making that resulted in two quite small cups of the kind then known as "petroti" or "stoneware" fetching a sum of 6000 sesterces.

LXVII. In our classification of glass we include also "obsian" ware, so named from its resemblance to the stone found by Obsius in Ethiopia. This stone is very dark in color and sometimes translucent, but has a cloudier appearance than glass, so that when it is used for mirrors attached to walls, it reflects shadows rather than images. Gems are frequently made of it, and we have seen also the solid obsidian statues of (the Roman emperor) Augustus of Revered Memory, for the substance can yield pieces

bulky enough for this purpose. Augustus himself dedicated as a curiosity four elephants of obsidian in the temple of Concord, while the Emperor Tiberius for his part restored to the cult of the Sun-god at Heliopolis an obsidian statue of Menelaus which he found included in a legacy from one Scius who had been governor of Egypt. This statue proves that the origin of the stone, which is nowadays misrepresented because of its similarity to the glass, is of an earlier date. Xenocrates records that obsidian is found in India, in Italy within the territory of the Samnites, and in Spain near the shores of the Atlantic. There is also the artificial "obsian" glass which is used as a material for tableware, this being produced by a coloring process, as is also the case with a completely red, opaque glass called in Greek blood-red ware. There is, furthermore, opaque white glass and others that reproduce the appearance of fluorspar, blue sapphires, or lapis lazuli, and, indeed, glass exists in any color. There is no other material nowadays that is more pliable or more adaptable, even to painting. However, the most highly valued glass is colorless and transparent, as closely as possible resembling rock-crystal. But although for making drinking vessels the use of glass has indeed ousted metals such as gold and silver, it cannot bear heat unless cold fluid is first poured into it; and yet glass globes containing water become so hot when they face the sun that they can set clothes on fire. Pieces of broken glass can, when heated to a moderate temperature, be stuck together, but that is all. They can never again be completely melted except into globules separate from each other, as happens in the making of the glass pebbles that are sometimes nicknamed "eyeballs" and in some cases have a variety of colors arranged in several different patterns. Glass, when boiled with sulphur, coalesces into the consistency of stone.

LXVIII. And now that we have described everything that depends upon Man's talent for making Art reproduce Nature, we cannot help marveling that there is almost nothing that is not brought to a finished state by means of fire. Fire takes this or that sand, and melts it, according to the locality, into glass, silver, cinnabar, lead of one kind or another, pigments, or drugs. It is fire that smelts ore into copper, fire that produces iron and also tempers it, fire that purifies gold, fire that burns the stone which causes the blocks in buildings to cohere. There are other substances that may be profitably burnt several times; and the same substance can produce something different after a first, a second, or a third firing. Even charcoal itself begins to acquire its special property only after it has been fired and quenched: when we presume it to be dead, it is growing in vitality. Fire is a vast, unruly element, and one which causes us to doubt whether it is more a destructive or a creative force.

10.1

Obsidian in Prehistory

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1 Introduction

According to the *Natural History* of Pliny the Elder [1], obsidian was a kind of glass found in Ethiopia by a Roman explorer named Obsius, a “stone very dark in color and sometimes translucent” but which “has a cloudier appearance than glass, so that when it is used for mirrors attached to walls it reflects shadows rather than images. Gems are frequently made of it.” At Pliny’s time, however, obsidian had already been long sought after as indicated, for instance, by its use for the pupils of Tutankhamun’s eyes in the funerary mask of the young pharaoh.

Obsidian is in fact a rather rare type of volcanic rock of little importance in the modern world, even to geologists (Chapter 7.2). It thus is infrequently listed in the indexes of geology reference volumes, even those specifically devoted to igneous rocks and their classification. Today, obsidian is used for some eye and heart surgical operations due to the fast healing rates of glass, and as a gemstone for jewelry and decorative objects where it may come from very far away: on the Italian island of Pantelleria, the geological-type location for Pantellerite, the irony is that a gift shop sells many items from Pachuca (Mexico)!

Of much greater significance is that obsidian was highly valued by prehistoric people in the form of lithic (flaked) materials that are among the most common artifacts in the archaeological record. They were the product of several distinct actions: acquisition of the raw material, preparation of a core for flaking, primary trimming, secondary trimming and shaping, use, maintenance or modification, and disposal. When flaked, obsidian produces extremely

sharp cutting edges and is often superior to chert, flint, jasper, and other lithic materials for cutting materials such as animal flesh and nonwoody plants.

Obsidian use for stone tools dates back to nearly two million years ago at early hominin sites in Ethiopia where standardized tools were produced in the Lower Pleistocene Acheulean. Significant quantities of obsidian have been found at later archaeological sites hundreds of kilometers away from their geological source, even when alternate lithic materials were available at lesser distances. These findings indicate that obsidian was selected for use because of its particular physical and visual properties and that the exploitation of such a valuable rock was by the way probably the cause of the initial human settlement of islands such as Lipari or Pantelleria.

Obsidian is playing a particularly special role in archaeology for several reasons: (i) it can be easily identified as a nonlocal material; (ii) it is relatively easy to determine the specific source of archaeological specimens through chemical analysis; (iii) its hydration, which develops over time, can be used to date directly the production of tools; (iv) its broad spatial distribution provides a means for investigating the interaction of different social or cultural groups, and to speculate on the parallel movement of materials that are not as well preserved in the archaeological record; and (v) it gives us the opportunity to examine the chronological developments and the dynamic nature of its usage by prehistoric peoples, and the economic and social conditions under which this usage occurred.

Starting in the early 1960s, elemental analysis of obsidian artifacts has been successful in identifying their geological source [2]. Since then numerous such studies have been performed around the world, using many different methods of analysis, so that the principles behind obsidian analysis and sourcing are well established [3]. On the other hand, development of nondestructive and portable instruments has overcome the restrictions imposed on obsidian

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analyses by many museums and governmental agencies, greatly enhancing the number of artifacts analyzed [4, 5].

To review these various features, this chapter will first summarize the geological context of obsidian formation and the reasons for their compositional differences. The main uses of this material, its resulting wear, and the manner artifacts can be dated will then be described briefly. More importance will be given to chemical compositions, which may be used to identify the geological origin of obsidian artifacts. The complex pattern of these sources will be illustrated for Europe and particularly for the western Mediterranean. Some examples of the conclusions drawn from these studies for prehistoric trade and ancient socioeconomic systems will be presented.

2 Geological Formation, Properties, and Sources

Obsidian is a naturally occurring glass with silica contents of 65–80 mol % and relatively high alkali contents (8–10 mol % of $\text{Na}_2\text{O} + \text{K}_2\text{O}$). There are two varieties, termed *calc-alkaline* obsidian (with high SiO_2 and relatively high CaO contents), and *peralkaline* (if the alkali total exceeds the Al_2O_3 content, also lower SiO_2 and CaO), deriving both from parent *rhyolitic* magmas (Chapter 7.2). Especially, the more typical obsidian with 75–80 mol % SiO_2 are so strongly polymerized and viscous that they cannot always complete their ascent up to the Earth's surface (Chapter 7.2). When they do so, instead of crystallizing as granite at shallow depths, their high viscosity then makes vitrification possible even for large blocks upon rather slow cooling.

That each obsidian source has its own chemical fingerprint in terms of minor and trace elements is the result of complex geological phenomena. First, SiO_2 -poor buoyant magmas form at depths of at least 100 km by partial melting of mantle rocks whose elemental composition can vary from one place to another. Then, during their ascent to the surface, magmas undergo a long process termed *magma differentiation* through which they give rise to residual melts progressively enriched in SiO_2 , alkali oxides, and some trace elements as a result of partial crystallization of dense, SiO_2 -poor minerals such as olivines $[(\text{Mg},\text{Fe})_2\text{SiO}_4]$ and pyroxenes $[(\text{Ca},\text{Mg},\text{Fe})\text{SiO}_3]$. In addition, chemical and physical interactions with a variety of surrounding fluids and rocks take place during the slow ascent of the magma so that in the end, even obsidian from successive flows of the same volcano can have different chemical fingerprints.

But geological obsidian is not as homogeneous as modern human-made glass because it frequently includes crystals and bubbles. In the form of tiny particles, magnetite (Fe_3O_4) is, for instance, often the first crystal to

form. Whether as isolated spherulites or as thick beds within the obsidian, crystals reduce the stone's ability to be flaked into a tool, as does exposure to groundwater that causes over long periods of time the formation of a white, hydrated amorphous phase called *perlite*.

In regions with the appropriate geological and geochemical characteristics, nearly all sources of usable obsidian are thus less than 20 million years in age. They are found in many places along the mountain chains of western North America and the Andes of South America; in southeast Europe, Anatolia, and the Middle East; on several Mediterranean islands; in East Africa; in northeast Asia and Japan; and on islands of Southeast Asia, Oceania, and the Pacific (Figure 1). Whether the obsidian is in primary or secondary geological contexts, these sources vary considerably in the magnitude and extent of the obsidian flow and in the size and quality of the obsidian blocks that are accessible (Figure 2).

Elemental composition, crystallinity, and the redox state of transition elements affect the color and transparency of obsidian, which are important visual characteristics and factors in their selection for use. Most are gray-to-black, while some are green, brown, and tan. A few examples of red, blue, yellow, and orange are also known. Obsidian is commonly dark because of the presence of nanometric crystals of iron oxides whose varying stoichiometries yield a variety of gray/black or mahogany hues. Like that of thick window glass, the green hue of peralkaline obsidian is due to the presence of ferrous Fe^{2+} at high concentrations (cf. Chapter 6.2). But since there is movement of the Earth's crust and cooling of the lava takes place under uncontrolled temperature and redox conditions, the microstructure of obsidian, and thus its color and transparency, can vary within a single volcanic complex.

3 Obsidian Use in Prehistory

As a glass, obsidian is very sharp and brittle, with a Mohs hardness of 5.0–5.5. This gives it both advantages (e.g. utility for cutting) and disadvantages (e.g. easy breakage) when compared with other stone material. First and foremost, it was used for stone tools, but also in some cases for jewelry or other decorative uses. Compared with other stones (flint/chert, quartzite, rhyolite, etc.), obsidian had significant cutting advantages, thanks to its glassy sharpness, especially for meat, hides, and other organic materials. Along with its visual distinctions, these characteristics often led to obsidian's selection over other available raw materials and to its resulting transport over great distances.

Obsidian from mainland sources was utilized very early on, with procurement ranges of at least 100 km for Lower Paleolithic people in east Africa and Eurasia. Including those in Japan, island sources appear to have been first



Figure 1 World map of obsidian sources utilized in ancient times. In the western Americas and eastern Asia, obsidians form in the geological context of compressive subduction zones by differentiation of andesite magmas. In other regions, they form from basaltic magmas in the extensive contexts of plate separation.

Figure 2 Balata dei Turchi (southern side of Pantelleria, Italy) primary obsidian flows (three arrows on left), with secondary deposits on slope in the lower right. Peralkaline obsidian, dark green, opaque.



used in the Upper Paleolithic (ca. 40–10 kya). Obsidian sources in the Americas were utilized starting with its Pre-Clovis inhabitants (>13 kya). In the Mediterranean, all of the island obsidian sources were regularly in use from the Neolithic period.

Some geological sources are fairly recent, coming, for example, from the volcanic outcrops in Lipari formed

about 8.5 kya ago [6], which were thus unavailable to the earlier residents of Sicily and peninsular Italy.

The discovery of obsidian artifacts has always been of importance to archaeologists, especially when there was no nearby geological source, as it indicates some kind of long-distance mobility or contact. The quantity or percentage of lithic artifacts made of obsidian, along with its

visual, physical, and chemical properties may be highly informative about ancient societies and how/why they obtained the raw material, produced finished objects, how and why they were used, and in what contexts they were left behind. In addition, other materials likely were transported in parallel to the obsidian.

4 Obsidian Studies

4.1 Typo-Technology

Typological and technological studies of lithic finds are necessary for full socioeconomic interpretations of

obsidian (and other stone tool) production and use. Starting with natural obsidian blocks, direct or indirect percussion may have been used for production of cores, often not far from the geological source, with the side effect of leaving behind large flakes and shatter (Figure 3). The cores may have been of specific types, for example, polyhedral blade cores, distributed over great distances to secondary production locations. The presence of smaller debitage and spent cores indicates such local production of tools. Certain tools were also retouched to enhance cutting properties. The production of stone tools requires some experience, as well as the intention to make specific types such as blades, scrapers,



Figure 3 Obsidian blocks (up to 40 cm in length), cores (up to 15 cm), blade (20 cm) and arrowheads (4–8 cm) from different parts of the Mediterranean.



and arrowheads, which would have been mounted on wooden or bone handles.

4.2 Use-Wear Studies

Macroscopic and microscopic examination of wear patterns on obsidian may be done to determine their actual usage, adding significantly to their archaeological context and associated materials [7]. In general, these patterns differ depending on the hardness (soft, medium, and hard) and siliceousness (animal, vegetal, and inorganic) of the worked material. Use-wear fractures are recorded as being absent, or at a rate of occurrence with fractures classified as flakes (conchoidal fractures), snaps, or steps. The distribution of edge-wear fractures is recorded as random or regular, and light or heavy, and complements width and edge rounding by wear fracture. The most likely function of a tool is determined from the type of use-wear, its frequency, size, and distribution. Owing in part to variations in the physical properties of obsidian from different geological sources, along with the actual use methods employed, experimental studies have been conducted in different parts of the world. In particular, it has been shown that there are quantitative and qualitative differences in wear patterns between obsidian from different geological formations, which may have influenced selection when material from more than one source was accessible [8].

4.3 Dating Methods

Obsidian hydration has been used in many parts of the world as a method to determine the date at which a tool was made from the rate of diffusion of water onto a freshly exposed surface. With a methodological approach begun in the 1960s, the thickness of the hydration rim or band may be measured by high-powered microscopy of a thin section (ca. 30 μm thick) [9]. The problem is that the rate of rim growth is affected by temperature, humidity, and pressure, as well as by the specific geochemistry and physical properties of the obsidian. To produce accurate age estimates, the recommended calibration thus consists of depositing a “standard” of freshly flaked obsidian in the ground for one year at a depth similar to that of the archaeological stratum along with a measurement device to determine the effective hydration temperature (EHT). The implicit assumption made is of course that these underground conditions did not change markedly since the obsidian was buried.

Another dating approach relies on secondary-ion mass spectrometry for depth profiling the hydration rim by direct measurements of the H concentration. Equations for the diffusion process are still being developed, but this analytical method is nondestructive and has the

additional advantages of incorporating the kinetics of the diffusion mechanism for water molecules and determining the saturation layer. Even more recently, infrared photoacoustic spectroscopy (IR-PAS) is being developed as an obsidian-dating method [10].

5 Provenance Analysis Methods

The characterization of obsidian begins with macroscopic observations and measurements of physical properties including color, transparency, density, and the presence of large crystals (phenocrysts). Whereas these features might have been important for obsidian users, they often are insufficient by themselves for reliably defining individual origins when multiple sources of obsidian exist in a particular region. One exception to this rule is the regional presence of a single peralkaline (green) obsidian source, for example, Pachuca in Central America and Pantelleria in the western Mediterranean. Another exception is found when there is a single source with large “snow flake” phenocrysts of cristobalite, for example, Giali in the Aegean. In some cases, microscopic analysis may differentiate sources from features such as crystal dimensions, frequency, and orientation patterns (streaks, linear, and random).

Whereas many methods of scientific analysis have been successful in distinguishing among sources in a particular region, the analysis of archaeological artifacts is often limited if the method is destructive or costly and if the artifacts must be taken outside a museum since museums and government agencies increasingly forbid destructive methods and limit analyses in external laboratories. Some countries do not allow artifacts to be sent beyond their borders, even if they do not have the analytical instrumentation needed.

The conservation and preservation of archaeological materials is actually of great long-term importance, in particular for obsidian put on display in museums, or involved in multiple studies including technology, typology, use-wear, and dating, as well as the large assemblages stored in warehouses. And even though the depth and quantity of obsidian artifact analyses has changed significantly since the first studies of the 1960s along with the development of many instrumental methods of analysis (Table 1), they vary considerably in different parts of the world because research funding for archaeology is generally limited relative to other disciplines.

A broad variety of analytical methods have nonetheless been successful in distinguishing geological obsidian sources from elemental or isotopic composition, geological dating, and magnetic properties. Within a single region, the volcanic events that produced obsidian may

Table 1 List of analytical sourcing methods.

Method	Sample ^a	Measurements	Limitations
<i>Dating</i>			
Argon–Argon (Ar–Ar) or Potassium–Argon (K–Ar) dating	Yes	Date of formation	
Fission-track (FT) dating	Yes	Date of formation	
<i>Isotopes</i>			
Thermal ionization mass spectrometry (TIMS)	Yes	Sr isotope ratios	
<i>Magnetic properties</i>			
Susceptibility and magnetometer instruments	No	Magnetic susceptibility, remanent magnetization	Need outcrop database
<i>Elemental</i>			
Atomic absorption spectroscopy (AAS)	Yes	Major/trace elements	
Electron probe microanalysis (EPMA)	Maybe ^a	Major/minor elements	Surface analysis
ICP mass spectrometry (ICP-MS) (quadrupole)	Yes	Major/trace elements	
With laser ablation (LA-ICP-MS)	Maybe ^a	Major/trace elements	Surface analysis
ICP atomic/optical emission spectroscopy (ICP-AES, ICP-OES)	Yes	Major/trace elements	
Instrumental neutron activation analysis (INAA)	Yes	Trace elements	Few major elements
Optical emission spectroscopy (OES)	Yes	Major/trace elements	Few major elements
Proton-induced X-ray/Gamma ray emission (PIXE/PIGME)	Maybe	Major/trace elements	Surface analysis
Scanning electron microscopy (SEM-EDS)	Maybe ^a	Major/minor elements	Surface analysis
X-ray fluorescence (XRF) (energy dispersive)	Maybe ^a	Major/trace elements	Surface analysis
Portable (or handheld) X-ray fluorescence (pXRF)	No	Major/trace elements	Surface analysis

^a A sample must be taken for solution, powder, or to fit within a chamber (depending on the size).

differ by hundreds of thousands or millions of years and be dated precisely by potassium-argon dating, which relies on the decay of ^{40}K into ^{40}Ar with a half-life of 1.25×10^9 years, or by the more sophisticated ^{40}Ar – ^{39}Ar technique. These methods, however, are not only expensive but also destructive so that they are rarely used on artifacts. Fission-track dating is another method that is based on the density of fossil damage tracks left within the atomic network of the artifact through atom bombardment by the alpha rays emitted when uranium isotopes decay radioactively. It has been used to some extent in determining formation ages, but the total number of artifacts tested is limited. Strontium isotopes (87/86) and magnetic properties (conferred by the permanent magnetization acquired by magnetite crystals upon cooling below their Curie temperature in the Earth's magnetic field) also have been shown to be successful, but remain rarely used.

The compositional homogeneity of a given obsidian source, coupled with significant differences between

different flows, has resulted in highly successful differentiation from certain elements, either major (i.e. with oxide abundances higher than 1 mol %) or in trace at lower contents. Referring to Chapter 5.1 for a review of these analytical methods, we, for instance, note that since the 1970s both X-ray fluorescence (XRF) and neutron activation analysis (INAA) have been widely used in obsidian studies. Inductively coupled plasma mass spectrometry (ICP-MS) methods were added in the 1990s (first archaeological use of ICP-MS presented by the author at a conference in 1991); and portable (including handheld) XRF in the 2000s (Figure 4). Notwithstanding potential limitations regarding transport and destructivity, the analytical method selected for archaeological projects is often based on availability in local institutional facilities and on the cost involved. Nevertheless, obsidian sources can often be separated from simple X – Y or multivariate graphs of selected elements. For example, in both Mesoamerica and in the Aegean/Central Anatolia, scatter plots with just Sr, Rb, and Zr clearly separate the existing groups [11, 12]).

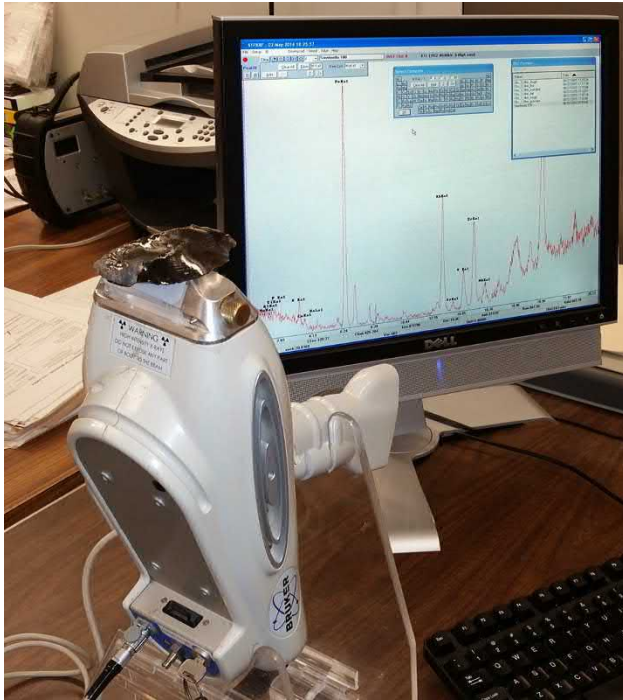


Figure 4 An obsidian sample sitting on a portable XRF instrument for the desktop nondestructive analysis of trace elements. The four most intense fluorescence bands shown on the computer screen are those of Fe ($K_{\alpha 1}$), Rb (K_{α}), Y (K_{α}), and Zr (K_{α}).

6 The Issue of Obsidian Sources: The European Region

For Europe, obsidian sources are limited to the Carpathian Basin (Slovakia, Tokaj Mountains of northeastern Hungary, and southwestern Ukraine); the Italian islands of Lipari, Palmarola, Pantelleria, and Sardinia; and the Greek Aegean islands of Melos, Giali, and Antiparos. The nearest other sources are in central and eastern Anatolia and the Caucasus, and on Tenerife in the Canary Islands.

For the central Mediterranean obsidian sources, there is considerable variation in color, transparency, and other visual characteristics, which may allow assignment of artifacts to a specific island, depending on the location and time period. Whereas Pantelleria obsidian is the only green (peralkaline) source, chemical analysis is still necessary to distinguish among the multiple subsources utilized there whose products were transported then to Sicily, Malta, and Tunisia. Lipari obsidian exists in both a highly glassy and transparent form (scale 4–5 out of 5) and in a mostly opaque form (scale 0–1) with numerous plagioclase feldspar $[(Ca_xNa_{1-x})Al_{1+x}Si_{3-x}O_8]$ phenocrysts. In Sardinia, the situation is more complex because of the existence of several Monte Arci subsources

with a variety of features [13]. The transparent SB2 (4–5 out of 5) is similar to type SA, and even to Lipari obsidian. SC sources are opaque and can be distinguished from type SA, which is transparent (4 out of 5), but not from SB1. Obsidian from Lipari and from these three Monte Arci subsources have been found at Neolithic sites in peninsular Italy, requiring scientific analysis for positive identification. In later periods (Copper and Bronze Ages), the SB1 and SB2 subsources appear not to have been used very much at all, so that a reasonable estimate of the percentage SA vs. SC may be made visually, albeit with some caution.

Elemental analysis, however, is highly successful in confidently distinguishing all Mediterranean sources and subsources (Figure 5) so that, starting in the 1990s, it has been widely used on large numbers of artifacts. Trace elements such as Nb, Rb, Sr, and Zr will separate all of the sources, as well as five subsources (different flows from the same volcanic complex) each for Sardinia [13] and Pantelleria [14], three each for Lipari [15] and Palmarola [16], and two for Melos [12]. The major elements Si, Al, K, Na, and Ca also can distinguish all of the Mediterranean sources, and some subsources (Figure 6).

The analysis of statistically significant numbers of obsidian artifacts and their assignment to the specific subsources utilized in former times is important in many cases, as these distributions relate to potential differences in the availability, quantity, quality, and features of the raw material. The relative importance of these sources may have changed over time at individual archaeological sites, whereas it also may vary between sites and even within sites based on the context (e.g. residential locations, ritual areas, and burials) [17]. Scientific analysis also is necessary to identify confidently “outliers,” for example, the finding of a few pieces of obsidian from Melos in the Adriatic, or from Sardinia in southern Italy, which have important significance in our understanding of long-distance contacts and trade not only of obsidian but likely other materials as well [18].

7 Obsidian Artifacts Studied in the Western Mediterranean

In the western Mediterranean, extensive studies have been done on obsidian sources and subsources, and on a large number of artifacts. This work includes a geological survey and characterization of the visual, physical, and chemical properties of the Monte Arci obsidian flows on Sardinia [13]. Elemental analysis of geological samples by INAA actually distinguished nine different subsources: SA, SB1a, SB1b, SB1c, SB2, SC1, SC2, and two others of unworkable size [19]. Conducting 200 analyses using

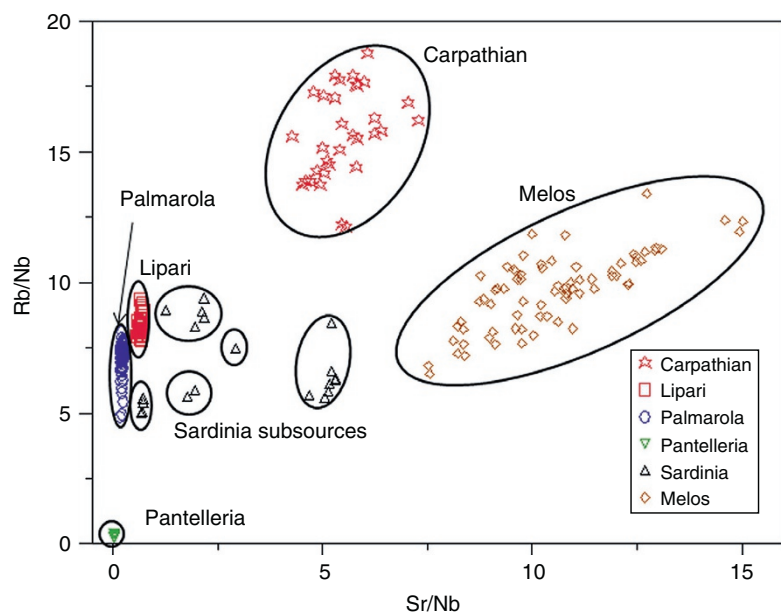


Figure 5 Trace element graph distinguishing Mediterranean obsidian sources.

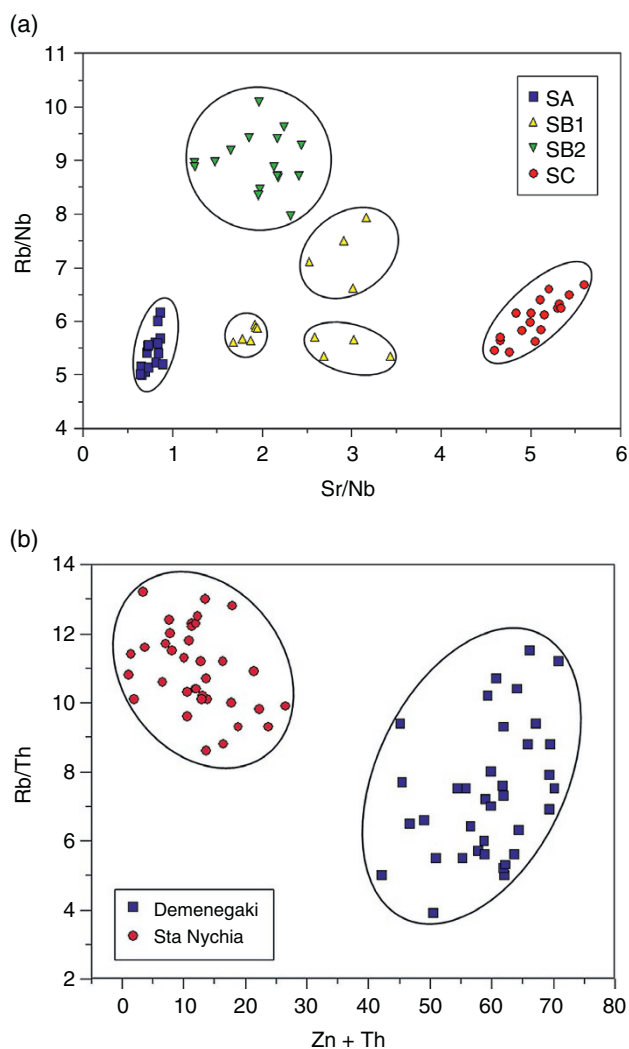
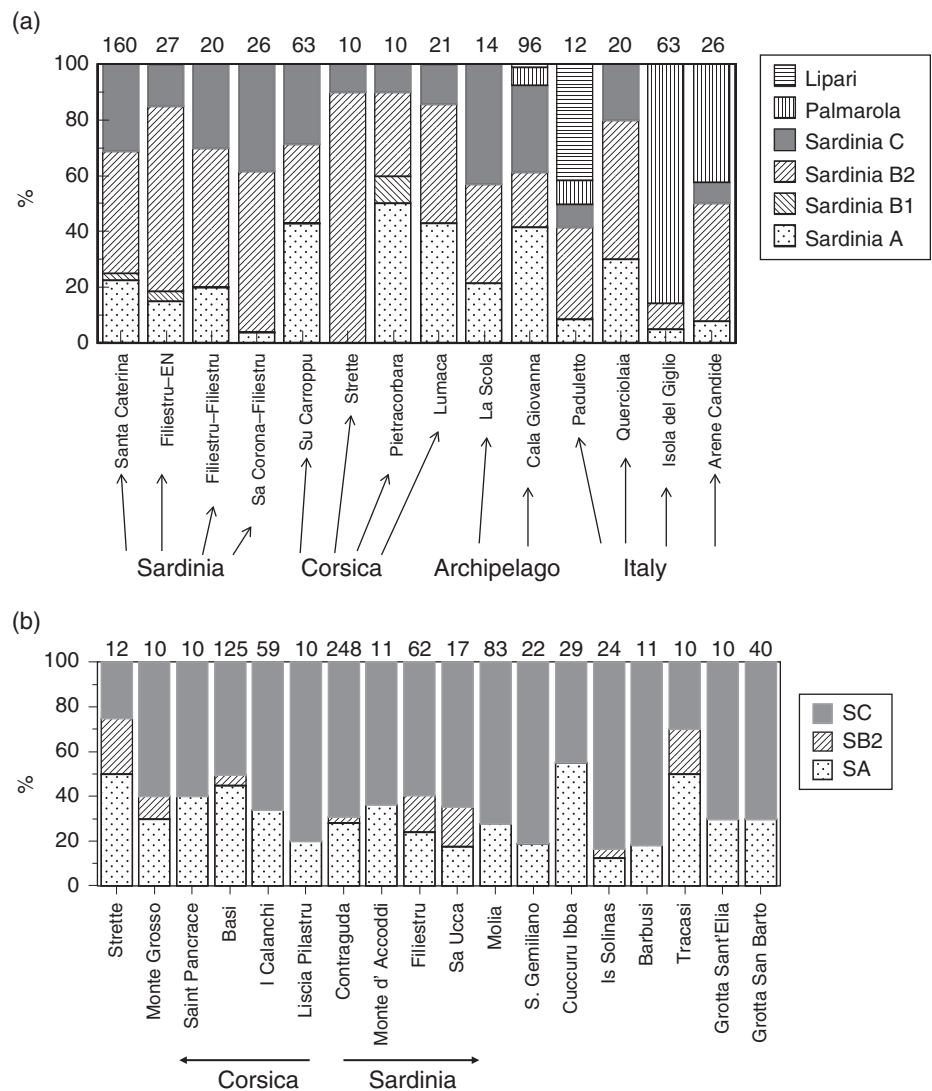


Figure 6 Multiple flows (subsources) may be distinguished on the islands of (a) Sardinia (Monte Arci) and (b) Melos.

ICP-MS in the early 1990s showed this method equally successful. However, given the tiny amount of SB1 obsidian having been used in the past, and the lack of visual/physical/geographic differences between SC1 and SC2, it was deemed unnecessary to distinguish these subgroups when addressing archaeological hypotheses of usage. Since the SA, SB1, SB2, and SC subsources could be distinguished in electron-microprobe analyses with wavelength-dispersive spectrometers, this minimally destructive and relatively low-cost method was used on 800 Neolithic and Bronze Age period (ca. 6000–1000 BCE) obsidian artifacts. The averaged results obtained on the 30- μ m spots analyzed showed that the three main subsources (SA, SB2, and SC) were widely used in the Early Neolithic period, and that by the Late Neolithic, SB2 was no longer in use while SC dominated most assemblages [17] (Figure 7). This pattern was confirmed by later studies at a large number of different sites in Sardinia and Corsica. Detailed geological survey was also conducted on the other Italian island obsidian sources (Lipari, Palmarola, and Pantelleria). Extensive chemical analyses of geological samples by INAA, LA-ICP-MS, and XRF revealed three subgroups each for Lipari [15] and Palmarola [16], while confirming five subgroups for Pantelleria. Laser ablation ICP-MS was chosen for the analysis of several hundred obsidian artifacts from Pantelleria, Corsica, and mainland Italy sites, due to it being minimally destructive on these small artifacts. The results expanded our understanding of the chronological change in Monte Arci subsurface usage, along with Lipari and Palmarola obsidian in mainland Italy. Research on obsidian in the western Mediterranean continues in southern France, Corsica, and mainland Italy.

Since 2007, a portable handheld XRF spectrometer has been used instead, mostly conducting the analyses within

Figure 7 Bar chart showing source frequencies for Early Neolithic (a) and Late Neolithic (b) sites in the western Mediterranean.



museums or government storage facilities in Sardinia, Sicily, Malta, different parts of mainland Italy, and in Croatia (Figure 8). The portability, nondestructive nature, and relatively lower cost of this instrument has allowed the analysis of over 10 000 obsidian artifacts so far, identifying some surprising patterns of usage, as well as unexpected outliers [5, 18].

One major surprise is the pattern of Lipari and Pantelleria obsidian use on the two main islands of Malta. At the mostly residential site of Skorba on Malta, 79% of the obsidian is from Lipari, and 21% from Pantelleria, whereas at the ritual and burial site of the Brochtorff Circle on Gozo, 72% are from Pantelleria and only 28% from Lipari. This major reversal is likely related to the specific purpose and usage of the obsidian at these two sites. Furthermore, the Pantelleria obsidian came from multiple subsources, while all of the Lipari obsidian was just from the Gabelotto subsurface. Some obsidian artifacts from

the Canneto Dentro subsurface have been identified, however, at sites in Sicily [5].

8 Obsidian Trade and Socioeconomic Systems

The ability to identify specific geological outcrops from which obsidian was utilized in prehistoric times, and to conduct analyses on large numbers of artifacts, has allowed archaeologists to test hypotheses about trade, transport (terrestrial and maritime), and about the socioeconomic systems involved and their changes over time. In this millennium, studies have been flourishing as a means to address broader archaeological research questions devoted, for instance, to procurement methods and spatial distribution, contact between different

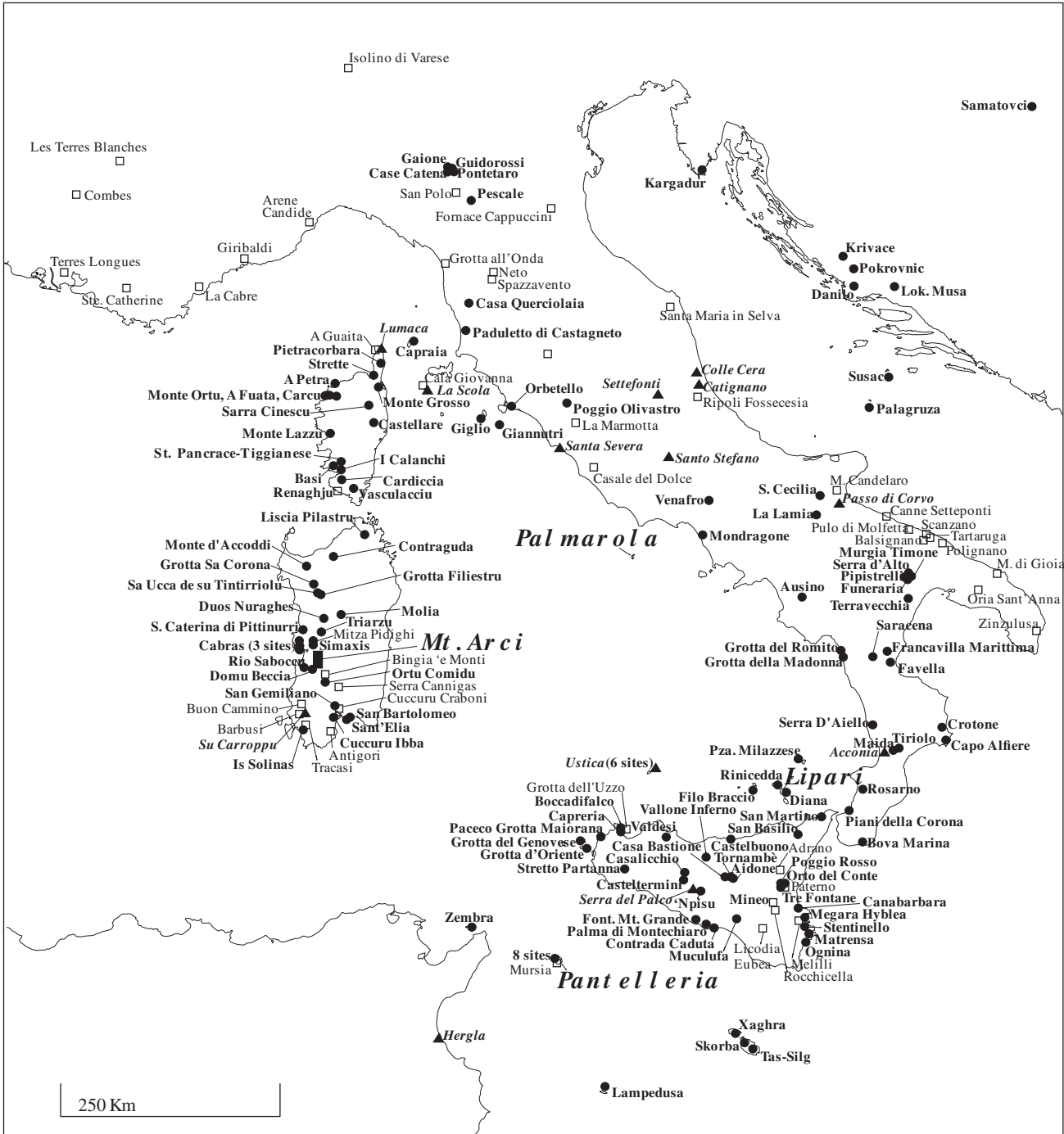


Figure 8 Sites with 10 or more artifacts tested (circles by the author, squares by others, triangles by both).

cultural groups, obsidian as a marker of cultural identity, and inferences about the movement of people and other materials [20].

Notable changes have occurred over time, which include access to island sources during the Holocene, development of territorial control and specialist production in later times, and symbolic and ritual use in some

complex ancient and historical societies. One study, on Epi-paleolithic and Early Neolithic obsidian at the site of Kortik in southeast Anatolia, shows heterogeneity on the local and regional scale in raw material selection from different sources and the technology used in this part of the Fertile Crescent [21], whereas another on the Bronze Age in the same region suggests that obsidian cores and

preforms, rather than finished tools, were distributed to local specialists for production of blades [22]. Similar social network issues have been addressed for sites in prehistoric Peru, most likely related to the development of more complex exchange systems by the Nasca, where economic models based on the proximity of obsidian sources have considered elevation and river location changes over time [23]. As for Mesoamerica, changes over the Preclassic, Classic, and Post-Classic Maya period resulted in a highly commercialized economy that does not conform with presumptions often made about preindustrial systems [24]. Archaeological sites are still being discovered and excavated, not just in developing countries in Africa, the Near East, East Asia, and Latin America, but even in settled areas of Europe. One example is the Middle Neolithic site of Terres Longues, at Trets, near Marseilles and the Mediterranean coast, where more than 4500 obsidian artifacts were recently excavated. This accounts for 90% of all obsidian artifacts found so far in France, combining discoveries of obsidian at more than 60 other prehistoric sites [25]. The study of such a large assemblage reinforces the previous evidence that Sardinian type A obsidian dominated this region, while the much higher percentage of obsidian in the lithic assemblage at Terres Longues suggests it might have been a redistribution center.

9 Conclusions and Closing Perspectives

Obsidian has long been an important raw material because its glass-like physical properties made it distributed far away from its geological sources until the advent of metals caused its various advantages to fade away. Scientific analyses have been developed for identifying the origins of individual artifacts and studying their use. More and more studies are multidisciplinary, and integrate the scientific analyses with the archaeological contexts, chronology, lithic typology, and usage studies. But while extensive research has been done in some parts of the world, there remain many areas where the geological sources have not been fully identified and thoroughly studied, and/or large numbers of obsidian artifacts have not yet been analyzed. Doing so for significant-sized lithic assemblages can lead to a fundamental understanding of ancient technological, economic, and cultural practices and how they changed over time.

The International Association for Obsidian Studies (IAOS: <http://members.peak.org/~obsidian>) is a professional organization, and international obsidian conferences have been held in Greece, Japan, Italy, and Hungary. Public interest in obsidian has increased, with

a major museum and center for obsidian studies established in Japan (www.meiji.ac.jp/cip/english/institute/obsidian.html) and one in Italy (www.museossidiana.it), along with many museum exhibits that include obsidian artifacts.

Acknowledgments

I thank many agencies in Italy, France, Malta, and Croatia for allowing my obsidian studies, and the many colleagues who have assisted me with these analyses, while I will always remember Miriam Balmuth who first got me involved in obsidian research more than three decades ago. Thanks are also due to Kyle P. Freund and Michael D. Glascock for their comments on this chapter.

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10.2

Ancient Glass, Late Bronze Age

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1 Introduction

The exact place where the techniques for the manufacture of glass were discovered is obscure. Even the date of the first glass production is uncertain. What is clear is that by the mid-fourteenth century BCE, glass was relatively common among the elites of Egypt, the Near East, and Greece [1, 2]. Before this time, however, there is a scattering of earlier glass objects stretching back to the third millennium BCE. These findings have been reviewed by several authors but there is some disagreement on the authenticity of certain pieces [1]. Some may be later artifacts that have become mixed with objects from earlier contexts either during the excavation or in early museum collections, whereas other pieces classified as glass may actually be faience.

What is clear, nonetheless, is that man-made glasses have apparently been found in secure contexts from the third millennium BCE and early second millennium BCE [3]. These include a pale yellow-green bead from Tell Judeideh (Syria) that dates from early in the third millennium BCE, a blue glass lump from Eridu (Low Mesopotamia) that has been confidently dated to the Akkadian period (2350–2150 BCE, Figure 1), and scatters of beads from perhaps as early as the Predynastic in Egypt (fourth millennium BCE) and through the Near East a little later. Lucas and Harris [4] stated that there is “no doubt whatsoever that glass beads and tiny glass amulets date from as early as the Fifth Dynasty [in Egypt, 2494–2345 BC], and it is exceedingly probable that they were all of Egyptian manufacture.” But Lilyquist and Brill [5] pointed out that these many beads are often “imperfect” with quantities of

quartz and other minerals entrained within them. They summed up the opinion, which is still held by present scholars, that “glass can only surely be said to appear at the end of the Second Intermediate Period (Dynasties 15/17) or beginning of Dynasty 18, ca. 1550BC.”

Glass, therefore, appears as scattered artifacts in early contexts before what would have been its main invention and the subsequent innovations of its making in the sixteenth century BCE. Because it was a highly valued material, ancient glass may be a rich source of information on Late Bronze Age (LBA) civilization through analyses performed to determine how and where it was made. The second question has in fact a wider interest in archeology than the first: questions of ancient technology are a specialist field, whereas if a precious material such as glass can be shown to have crossed borders, it will reveal connection between powers, exchange, or trade with perhaps much wider implications.

Hence, scientific work on the provenance of glass is now dominating over the investigation of technical questions of production. In this chapter, the various tools used for this purpose will be reviewed. The first is analyses of chemical composition, which have long been practiced to identify specific glass families. Many problems cannot be solved on the basis of composition only, however, so that advantage can also be taken of the often heterogeneous nature of ancient glass to draw additional information from microstructure as investigated by scanning electron microscopy (SEM, cf. Chapter 2.3). As extensively determined in geochemistry since the 1950s, variations of the abundances of either stable or radiogenic isotopes represent yet other tracers of past phenomena with an unprecedented resolution whose application to glass studies will thus be illustrated. But a few words about the origins of early glass are appropriate before describing how these three methods are applied to a variety of problems.

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Figure 1 Blue glass lump from Eridu, believed to date to the late third millennium BCE ($3.8 \times 3.4 \times 3.3$ cm; British Museum, BM 115474). Source: © The Trustees of the British Museum.

2 Early Glass: From Faience to Glassmaking

The early objects were all small. Many, if not most, contain glass that is imperfect. Following the argument of Lucas and Harris [4], it is very tempting to see these objects as by-products of the glazing material deposited on stone and faience, two well-established products across the Mediterranean and beyond (Chapter 10.6). The powders used in glazed stone and faience is thought to have been made up of the same raw materials as the later glass. Errors in the manufacturing process could relatively easily have led to the production of small amounts of imperfect glass, which would have been worked into the occasional bead or amulet alongside the more normal faience. Peltenburg [1] saw this evolution as two clear stages of glass production: Stage 1, where the unique properties of glass were not realized yet so that glass was infrequent and irregular, and Stage 2, where glass was deliberately produced and its properties exploited. Peltenburg argued that the most significant change between the two stages was the ability to work the glass hot to create larger objects and vessels, and he has linked this feature with the only other

industry that manipulated material at high temperatures, metalworking.

However, Shortland [2] has contended that glass could, and was, manipulated cold, with stoneworking technologies, so that the important step might just have been a greater desire for glass, rather than necessarily any technological jump. The fact is that the rise of glass coincides with the beginning of the states of the Near East and Egypt regarding themselves as imperial powers. This new situation led to campaigns, conflict, and competitive gift giving on a huge scale, in which glass played a part. In this period, glass was regarded as a precious material, of equal value to lapis lazuli and turquoise, and exchanged as such. Gift lists and temple offertory scenes show glass being given and the value in which it was placed [2]. Perhaps this political reality of the new times meant that glass had a new “market” for use that drove the innovation.

Whatever the cause of the innovation, glass starts to appear in quantity in archeological contexts of the fifteenth century and by the fourteenth is widespread, but never common, in keeping with its high value. Where the first manufacturing sites for glass were located is again unclear and the former glass production sites identified remain rare. It is probable that the production of glass objects was in two stages, *glassmaking*, where glass ingots or chunks were produced from raw materials, and *glassworking*, where this glass was worked into finished objects [6]. Certainly, it has been strongly argued that in later periods these operations could, and were indeed usually taking place on separate sites some distance from each other (Chapter 10.3). The conventional argument is that the first glassmaking factories were in the Near East, probably in what is now Northern Syria [3]. It is based on some early finds of glass vessels in this area, and also on finds from the site of Nuzi, near modern Kirkuk, which had large amounts of glass connected with a destruction level evident in the temple and palace complexes and was dated to the fifteenth century BCE. Because modern scholarship now puts this destruction level in the middle of the fourteenth century BCE, it is now less clear that the Near Eastern glass predates that of Egypt. Either could have had the first glass factories.

The picture is complicated because no glassmaking sites are known from the Near East [2, 3]. The two earliest sites known are in Egypt. Malkata is on the west bank of the Nile, dates from the early years of the fourteenth century BCE, but the full excavation has never been properly published. The earliest really good evidence therefore comes from Amarna, in middle Egypt, where it is probable that glass was made and certain that it was extensively worked. Much of our knowledge of glass production in the LBA is drawn from this site and the slightly later Qantir [7, 8].



Figure 2 Heart amulet, Egyptian 18th Dynasty, late fourteenth century BCE (2.7 × 1.9 cm; British Museum, EA 65542). Source: © The Trustees of the British Museum.



Figure 3 Inlay, Egyptian from Thebes, 18th dynasty (33 × 26 cm, British Museum EA 64217). Source: © The Trustees of the British Museum.

Although the most common objects were glass beads, amulets (Figure 2) and inlays (Figure 3) were also important. The material is almost always brightly colored, colorless glass being relatively rare but nevertheless present.

In any case, it is the glass vessels that stand out and are probably the most iconic objects of glass in the LBA (Figure 4). They are striking objects and always would have been, partly because of their beautiful color: they are typically blue bodied with trailed and marvered decoration in contrasting blues, yellow, and/or white. These objects passed down to us almost unweathered and unchanged in many of the Egyptian vessels. Most of them are small, averaging around 10–12 cm in height. Their exact use is unclear. They are found in elite contexts such as palaces, temples, and the tombs of the King and his court. They probably contained precious oils and resins and some at least were associated with toiletry boxes and make up [4].

3 Chemical Composition: The Analytical Standpoint

From a scientific standpoint, attention first turned to the chemical composition of ancient glass (cf. Table 1). Especially for Egyptian products, this interest stretches back to the eighteenth century [4]. Although some early work by wet-chemical analysis was carried out in the nineteenth century, it was not really until the middle of the twentieth that a concerted effort relied on scientific analysis to investigate composition and formation processes. The most important of this work was done by W.E.S. Turner (see Chapter 10.11), whose six published papers in the *Journal of Glass Studies* between 1954 and 1959 set the standard for further investigations, especially on the changes in chemical composition and raw materials [10].

Over the last two decades the amount of analytical work carried out on LBA glass has greatly increased. This has come about for a variety of reasons. Firstly, the development of new techniques requiring very small sample sizes such as LA-ICPMS (Chapter 5.1) has meant that the range of objects that can be analyzed has greatly increased. Secondly, new developments, particularly in the isotopic analysis of glass, have meant that new theories and possibilities could be tested. Lastly, the number of groups involved in analysis has greatly increased, bringing more papers and more interest into the area.

The key questions asked to the analytical specialist by historians and archeologists working with glass are those that Turner was trying to answer in the 1950s: How was it made? Where was it made? The work has therefore addressed the technology of glassmaking and glassworking and the provenance of individual glass vessels and ingots.

The technology of glassmaking starts with the selection and gathering of the raw materials, their transport, and storage. The manufacturing facility then needs equipping with furnaces, crucibles, tools, fuel, and staff. The molten glass then has to be molded into ingots or cooled and broken into cullet for transport. Most of the scientific work

(a)



(b)



Figure 4 (a) Egypt (cosmetic jug, 18th dynasty, 24 × 30 cm; British Museum 22819); (b) Ur, Mesopotamia (fluted glass bottle, height 11.8 cm; BM 120659). Source: (a, b): © The Trustees of the British Museum.

has concentrated on the analysis of the raw materials and the technology that was used to convert them into glass. The main analytical tool used for this work has been the scanning electron microscope (Chapter 2.3) with an attached energy-dispersive spectrometer (SEM-EDS). Thanks to its imaging (SEM) and compositional (EDS) capabilities, SEM-EDS actually is an ideal tool for the initial work on glass of all periods, but perhaps especially on early glass. Work started on polished cross sections of the glass and glassmaking debris. It has since then developed into analyses of small stub-mounted samples with environmental SEM, which even allows analysis of complete objects to be made without needing to coat them with carbon or gold.

As a nice complement to SEM-EDS, the microprobe SEM-WDXS can also be used ([11], Chapter 10.3). The SEM imaging systems on most microprobes are not optimized, or even absent altogether, so obtaining good images is better left to a proper SEM. In contrast, the analytical abilities of the microprobe, in terms of precision,

accuracy, and limits of detection, with certain limitations, are better than for an SEM. A combination of better quality SEM-EDS analyses with newer systems combined with reliable microprobe analyses of more minor and some trace elements has enabled more work on colorants to be undertaken and new hypotheses on the sources of the raw materials used for glassmaking and on their mineral or metallic nature to be formulated.

Regarding isotopic analyses aiming at provenancing of archeological artifacts, it is beyond the scope of this chapter to review the chemical principles and analytical methodology. In summary, these analytical procedures utilize well-established chemical methods of acid dissolution and ion-exchange chromatography for the isolation and purification of microgram quantities of target element from the sample. By using laser ablation, one can strongly reduce the sample consumption so that artifacts can be analyzed in a quasi-nondestructive way, a development with great prospects in archeological research, where

Table 1 Typical compositions of glasses from the Late Bronze Age [9].

(a) Major elements															
		SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	FeO	TiO ₂						
Egypt	Colorless	64.7	0.8	9.3	4.3	17.5	1.7	0.3	0.07						
Egypt	Cu blue	65.5	1.4	8.8	3.8	14.7	2.8	0.8	0.11						
Egypt	Co blue	61.6	2.2	7.0	4.0	20.9	1.3	0.4	0.05						
Egypt	Opaque blue	59.5	0.7	9.4	4.9	18.1	2.0	0.4	0.06						
Egypt	White	60.7	1.1	8.2	4.1	19.5	2.3	0.5	0.07						
Egypt	Yellow	58.4	0.8	9.6	4.2	16.7	1.8	0.6	0.05						
Egypt	Green	60.6	0.7	8.2	4.0	18.8	1.5	0.4	0.10						
Egypt	Purple	63.6	0.7	9.7	4.4	16.5	2.1	0.5	0.06						
Nuzi	Blue	68.2	0.5	8.6	3.8	13.9	1.9	0.2	0.01						
Nuzi	Opaque blue	63.1	0.5	8.7	3.2	17.0	3.0	0.3	0.02						
Tell Brak	Blue	64.4	0.6	5.7	4.3	18.9	3.2	0.5	0.02						
Tell Brak	Opaque blue	64.6	0.2	8.5	3.0	17.4	1.8	0.1	0.03						
(b) Minor elements															
		CoO	CuO	MnO	NiO	ZnO	As ₂ O ₃	SnO ₂	Sb ₂ O ₃	BaO	PbO ₂	Cr ₂ O ₃	P ₂ O ₅	SO ₃	Cl
Egypt	Colorless	0.01	0.00	0.02	0.00	0.01	0.01	0.02	0.01	0.03	0.01	0.00	0.13	0.32	0.75
Egypt	Cu blue	0.02	0.75	0.03	0.00	0.05	0.00	0.03	0.04	0.04	0.02	0.03	0.17	0.12	0.79
Egypt	Co blue	0.20	0.04	0.23	0.18	0.25	0.02	0.01	0.00	0.03	0.04	0.01	0.19	0.42	0.97
Egypt	Opaque blue	0.03	1.33	0.04	0.03	0.00	0.10	0.15	1.96	0.04	0.00	0.00	0.14	0.30	0.86
Egypt	White	0.01	0.02	0.04	0.03	0.02	0.05	0.01	2.00	0.04	0.03	0.00	0.20	0.30	0.89
Egypt	Yellow	0.02	0.03	0.02	0.00	0.27	0.01	0.01	0.64	0.03	5.48	0.00	0.18	0.40	0.80
Egypt	Green	0.01	1.42	0.04	0.01	0.15	0.01	0.11	0.15	0.05	2.44	0.02	0.13	0.33	1.01
Egypt	Purple	0.02	0.10	0.79	0.06	0.00	0.00	0.00	0.04	0.04	0.02	0.02	0.17	0.36	0.84
Nuzi	Blue	0.01	1.49	0.04	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.26	0.31	0.56
Nuzi	Opaque blue	0.00	0.96	0.03	0.02	0.01	0.02	0.00	1.29	0.01	0.00	0.00	0.51	0.31	0.98
Tell Brak	Blue	0.02	0.98	0.04	0.02	0.04	0.07	0.01	0.02	0.00	0.01	0.02	0.16	0.27	0.87
Tell Brak	Opaque blue	0.00	1.22	0.02	0.02	0.02	0.04	0.02	2.10	0.00	0.03	0.04	0.13	0.29	0.62

sampling of an object may be problematic. To exclude contamination, the chemical preparation of the material sampled is done in a clean lab environment where necessary.

4 Material Sources

4.1 Raw Materials

The EDS has the capability of analyzing most elements heavier than carbon. It can, therefore, detect more than 99% of all the elements that are present in LBA glasses. The detection limits for most elements can be around 0.1% or less in ideal circumstances. Small samples can be taken and polished blocks produced that are an excellent target for the analysis. The required sample size can be much smaller than for wet-chemistry or atomic-absorption-type techniques, and the sample is preserved so it can be imaged too.

Studies with the SEM-EDS in the early 1980s expanded on the earlier work of Turner and others to give a clear idea of the raw materials used in the earliest glass. They showed that all glass of this period is of a quite uniform soda-lime-silica composition, typically 16–21 wt % Na_2O (*soda*), 4–5% CaO (*lime*), and 58–68% SiO_2 (*silica*). In addition, significant amounts of magnesia (3–5% MgO) and potash (1.5–3.0% K_2O) are found, in stark contrast to almost all later Roman glasses where both oxides have typically much lower concentrations (Chapter 10.3).

Turner [9], supported by later SEM work by Lilyquist and Brill [5] and others, suggested that this clear pattern was caused by the use of different raw materials, specifically different silica and soda sources. Silica must have been derived from a sand, pebbles, or rock source. Pure, or nearly pure, silica sources that are needed for the production of glass have very high melting temperatures, hundreds of degrees above the 1100–1200 °C that would be the absolute maximum that an ancient furnace of this period could have reached. It was therefore necessary to add a flux to lower the temperature of melting. The differing compositions have therefore been interpreted universally as different silica source-flux combinations.

In the Roman period, a relatively pure soda flux was used in the form of sodium carbonate and related minerals from evaporitic lakes such as the Wadi Natrun in Egypt. This source was relatively low in magnesia and potash but resulted in a similar glass ([10], Chapter 10.3). In contrast, during the LBA, high-magnesia, high-potash glass is thought to have derived from the ash produced by the burning of halophytic plants, such as *Salsola* and *Salicornia*, which grow on the margins of deserts and in coastal areas. Interestingly, there is a third type of glass with low

magnesia and high potash values, sometimes known as “LMHK” [12], which has almost equal amounts of soda and potash. This glass type was restricted to the Bronze Age of Europe and overlapped temporally with the LBA glass of Egypt, Greece, and the Near East discussed here. Once again it appears to have used a different flux source, but in this case, this source has never been universally agreed.

4.2 Coloring Elements

Because most of the glass of this period is strongly colored, SEM-EDS has been valuable to identify the elements used for this purpose. A simple procedure consists in identifying the elements that are present in excess in colored materials with respect to colorless glass (cf. Chapter 6.2). Blue is the most common hue, which is generally caused by copper. Darker blues were achieved with cobalt, and occasionally with a mixture of cobalt and copper. White glasses have higher levels of antimony, and yellow glasses of both lead and antimony, which points to the presence of antimonate opacifiers. Opaque blue glasses colored with copper and/or cobalt may also have higher antimony, which suggests that they too had an opacifier. Green glasses contain copper, lead, and antimony, which indicates either a mixing of yellow and copper blue glasses, or the combination of the technology used in the production of each. Purple and black glasses had small and large amounts of added manganese, respectively, whereas red once more relied primarily on higher copper contents. Work on the composition of LBA glass has proven very valuable and has been supplemented by further systematic analysis with microprobe SEM-WDXS.

Instead of asking what the coloring element of a blue glass might have been – copper, as is well known for a majority of glasses – the question has moved to know how this element was added to the glass: was it as malachite $[\text{Cu}_2\text{CO}_3(\text{OH})_2]$, copper oxide, copper metal or bronze, scrap or pristine metal? For copper, it has been observed that some glasses contain traces of tin, as first noted with copper-blue faience. This feature seems to have been a characteristic of most, but not all, copper-blue glasses found in Egypt. The copper:tin ratio in the glass is about 10 : 1, roughly the same as in contemporary bronze metal, so it is possible that the colorant added to Egyptian glasses was bronze filings, scale, or metal. In contrast, tin is absent in glasses found in the Near East, so a copper metal or ore is more likely.

4.3 Opacifying Agents

Highly magnified images of glasses taken with the SEM have greatly added to the knowledge of glass colorants.

Imaging of the copper red glasses has, for instance, shown fine dendritic growths of cuprite (Cu_2O), giving the material its distinct color (Chapter 6.2). As for the aforementioned opacity in many glasses, it is caused by the presence of crystalline particles. White and opaque blue glasses are created by the presence of a fairly uniform spread of calcium antimonate whose morphology likely shows that they precipitated out of the glass itself. According to XRD analyses, the phase present is variable and complex and may relate to both the composition and cooling regime of the glass, which might have varied from a site or an area to another. Yellow and green glasses bear lead antimonate particles whose uneven distribution, along with their ragged and partially dissolved appearance, suggest that they formed first before being dispersed by stirring into the glass rather than precipitating out of it. These conclusions have been confirmed by experimental work that has shown that the calcium antimonate precipitates out of the glass in white and opaque blue colors, whereas the lead antimonate must be added and stirred in.

4.4 Frit or Not?

Besides, SEM imaging has been extensively used in attempts to identify and describe workshop debris, tools, and even intermediate steps in glassmaking. Excavations at Amarna in Middle Egypt in the later nineteenth and early twentieth centuries along with more modern excavations at Qantir [7, 8] have, for example, unearthed a range of debris that might have been involved in glassmaking. Early work by Petrie [13], followed up by analysis, suggested that the raw materials for glassmaking had been heated to drive off volatiles, or *fritted*, before being finally crushed and melted. Petrie identified vessels containing a blue vitrified quartz held together with glass, which he identified as *frit* remaining from this process. Work by SEM imaging combined with EDS showed that the composition was wrong, however, so that glass could not have been made from this *frit* without substantial additions of flux, which would have negated the point of the fritting in the first place. Hence, it is clear that this material was more likely involved in faience or pigment manufacture. Recent work on Amarna material has identified a frothy white opaque glass that may be a much better candidate as an intermediate stage in glass production.

4.5 Glass Working

Much of the analytical research has been accompanied by a good deal of experimental work of two different types: either detailed replication of usually single steps in the glassmaking process with modern kilns and mostly laboratory reagents, or experimental firings in the field

attempting to replicate the operation of ancient furnaces and other structures.

Whole furnaces have, for instance, been built in Egypt, along the lines of the ancient ones discovered at Amarna [7]. Doubt had been expressed that these quite large furnaces could not reach glassmaking conditions, but experimental work has shown that their design actually made temperatures in excess of 1000 °C possible. Of course, this conclusion does not mean that these furnaces were used in the manufacture of glass, but does dispel the doubt that in terms of temperature at least, they were capable of it.

Imaging by SEM of the vessels and furnaces that might have been used in glassmaking has in addition been carried out. The question asked here was that of the temperature at which furnaces were being fired. To answer it, the microstructure of cross sections of the furnace and vessels walls has been investigated by SEM and the observed fabrics compared with experimentally refired samples of clay from the same site. The closest match was then taken as indicative of temperatures of 1050–1100 °C.

The final products of *glassmaking* in this period were probably circular glass ingots. While rare in terrestrial excavations, a remarkably high number of 175 ingots were recovered from the LBA ship found at Uluburun, off the southern Turkish coast. These ingots were probably the normal form in which glass traveled, to be worked into finished objects at other sites.

Analysis of glass vessels by SEM has shown how this glassworking might have been carried out. The internal surfaces of the glass vessels are usually covered with the remains of a core, which was subsequently scraped out. With these core-forming techniques, a core of clay and/or dung was dipped into the molten glass to form the body of the vessel. One then decorated the vessel by trailing glass rods across the surface and marvering them flat. The trailed decoration forms a characteristic semicircular shape, which can clearly be seen in cross sections through the wall of the glass vessel examined under SEM.

5 The Issue of Provenance

The principal requirement of provenancing glass of any period is that there should be consistent variation in the composition of the finished glass between different primary glass manufacturing workshops. In some periods, this is relatively easy to see since the different fluxes used in different areas gave rise to markedly different compositions [10]. Unfortunately, however, the flux is all plant ash in the LBA of the area discussed here. Not only that, but within certain criteria, the composition of

the glass forms quite a wide spread, perhaps caused by variability in the raw materials and/or furnace conditions. In terms of major elements and most colorants, therefore, the glass looks very similar regardless of where it was found or made [14].

Regarding the identification of pigment sources in these early glasses, a breakthrough came in the 1980s when Kaczmarczyk [15] published an important paper on cobalt, a very strong coloring agent as only 0.1% CoO makes a glass distinctively blue (Chapter 6.2). Cobalt was introduced as a coloring agent in the LBA to be used in glass, faience, and as a pigment on ceramic vessels. Pointing out that cobalt-colored glasses were common in Egypt, but rare in the Near East, Kaczmarczyk hypothesized that the source of the cobalt colorant might therefore lie in Egypt. Not only that, but trace-element analysis by SEM-EDS of Co-colored glasses showed that where cobalt was present, the aluminum, manganese, nickel, and zinc levels of the glasses were also raised, suggesting that the cobalt colorant contained these other elements as well. Because cobalt minerals are rare, and native cobalt unknown, possible sources are relatively few so that Kaczmarczyk pointed to cobalt-bearing alums found in the Western Oases of Egypt as the source for the colorant. Experimental work has actually shown that they produce a good cobalt-colored glass. These glasses were thus made from an Egyptian pigment and largely restricted to Egypt (except some found in Greece, by [16], and other rare exceptions). But more recent work [17] has found other Co-colored glasses at Nippur, in the Near East, in which cobalt is associated with nickel, arsenic, and lead. This difference thus points to the existence of a second, unknown cobalt source.

Unfortunately, this approach has only really worked for cobalt colorants. For other colors, it has proved very difficult to differentiate production sites. Indeed, Jackson [14] said “glass from Egypt and Mesopotamia cannot be unequivocally distinguished on the basis of their chemistry.” This statement was demonstrated by a large survey of the glass by SEM-WDS. What was needed was a technique with lower detection limits, where not just 12–14 elements in the glass could be analyzed, but 35–40. The step forward came with the application of LA-ICPMS to the analyses of these glasses. The argument used in this analysis was that the composition of the glass should reflect that of the plant ash being used. It in turn would reflect the composition of the plant itself, which might vary depending on the soil in which it grew, itself dependent on the geology. The composition of the glass might therefore reflect the geology of the region in which it was made.

With this theoretical underpinning, accurate trace-element analysis of these glasses was carried out on the polished samples mounted in SEM blocks that had been

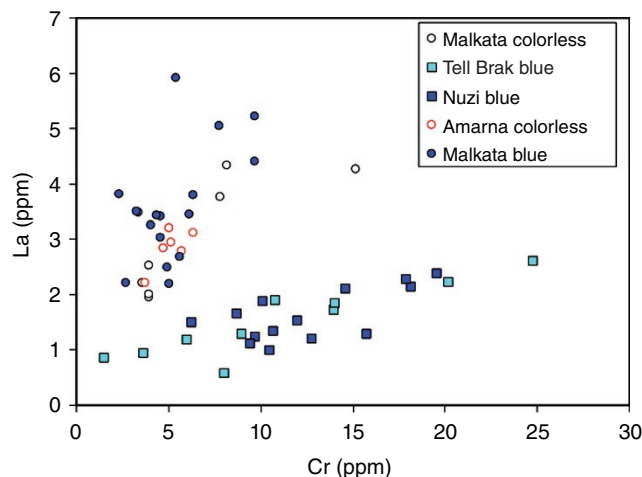


Figure 5 The clear distinction between glasses found (and therefore thought to be made) in Egypt (Amarna and Malkata) and in the Near East (Nuzi and Tell Brak) revealed by plots of ICPMS data for lanthanum against chromium.

used for earlier studies of the major element composition of the glasses. These made ideal sample mounts for LA-ICPMS, and allowed analyses to be performed down to sub-ppm levels for many elements. The results showed a consistent difference between glasses found in the Near East and in Egypt, the former having higher Cr/La and lower Zr/Ti ratios and the latter the opposite (Figure 5). It was speculated that this contrast would relate to the sources of clay in the areas – Egyptian Nile silts coming from granitic sources, whereas the clays of the great rivers of Iraq from more mafic (basaltic) sources.

Other papers have pointed out that the signature could be down to grinding debris incorporated in the glass when hard rock pounders of differing compositions were used in the grinding of the raw materials for the glass. Whatever the source, the pattern is consistent and has been seen in other glass of the same period from Greece and from the shipwreck at Ulu Burun, allowing these glasses to be provenanced to the Near East and/or Egypt.

6 The Isotopic Clues

6.1 Isotopic Analyses

More and more, the question “where glass was made?” is being addressed with isotopic analysis [18]. Even though the isotopic composition of the elements is assumed to be constant in nature, small variations do occur through several processes. For certain elements (e.g. Sr, Nd, Pb) the reason is that one or more of their isotopes is the end product of the decay of naturally occurring long-lived

radionuclides. Because they vary with time and the initial mother/daughter ratio, the isotopic composition of these elements are not used only for geochronological dating, but also to trace the sources of detrital matter in the sedimentary and biogeochemical cycles. Likewise, stable light elements (e.g. B, O) and even some heavier elements (Sb, Cu) display natural variations in their isotopic composition as a consequence of kinetic and thermodynamic isotope fractionation effects. Although these variations are often very small, they also reflect different origins and formation processes for raw materials.

Now, the important point in provenancing and/or source-tracing studies is that isotopic ratios in glasses depend only on those of the raw materials, and not on glassmaking processes, especially when the relative mass differences between the isotopes of the same element are small. In other words, the isotopic composition of the artifact is identical, within analytical errors, to that of the raw material from which it was derived, whereas the signatures of different raw materials used, and hence of the resulting artifacts, may differ.

6.2 Lead

Lead isotopes were the first (radiogenic) isotopes used to investigate ancient materials. Since the 1960s, they have, for instance, been extensively used in archaeometry to trace the provenance of metals, mainly from the Mediterranean Bronze Age period, even though their disadvantages have given rise to some controversy [19]. From the beginning, lead isotopes have also been analyzed in a range of archeological materials to distinguish between vitreous materials of different regions. Overlap was noted between “fields of origin,” however, as is not unusual with lead isotopes. In further studies, lead isotopes were used with varying success to link raw-material mixtures or regional signatures to glass production units. Low lead concentrations in glass, in the 10–100 ppm range, are likely to originate from non-quartz mineral constituents in the silica source, though low levels of lead have also been ascribed to impurities in plant ashes used as a flux. The discovery of a homogenous lead isotopic composition in a range of glass samples suggests that a homogenous silica raw material had been used, and perhaps that produced was made at a single location. Heterogeneous lead isotopic compositions of samples, particularly with high lead contents, are an indication of recycling of the glass or may be caused by the addition of a mineral compound to the batch as a colorant or opacifier, likely influencing or obscuring the original signal of the silica raw material. Opaque glass, in particular, could be studied to trace the origin of its lead, but such studies have not been performed yet.

6.3 Strontium–Neodymium

The application of strontium isotope analysis to ancient glass is based on the assumption that this element was incorporated with the lime-bearing constituents. Hence, strontium in LBA glass is principally derived from the plant ash used, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio having thus reflected the bioavailable strontium of the soil on which these plants grew, which in turn reflected the geological origin of the soil. Plant-ash glasses can have high strontium contents, which often show considerable variations, indicative of the varied or complex source of the element and the concentrating effect of ashing the plant. This feature illustrates how important it is to establish variations in Sr isotopic signatures in the landscape as part of trying to provide a provenance for plant-ash glasses. Conversely, the neodymium in glass is likely to have originated from impurities of the silica raw material. It is thus typical of the geological environment from which the silica originated. Correlations between Sr and Nd isotope ratios should thus allow the sources of both silica and flux to be distinguished.

This method has been successfully applied to Bronze Age glass from Egypt and Mesopotamia [20, 21], where multiple production locations were proven, each having used its own set of glassmaking raw materials. Even though glass was exchanged from one LBA Mesopotamian site to another, this production was entirely separated from the making of glass in Egypt (Figure 6). Glasses of this period identified as having been traded are indeed exceptional and are analytically proven only in rare cases [16] despite textual and archeological

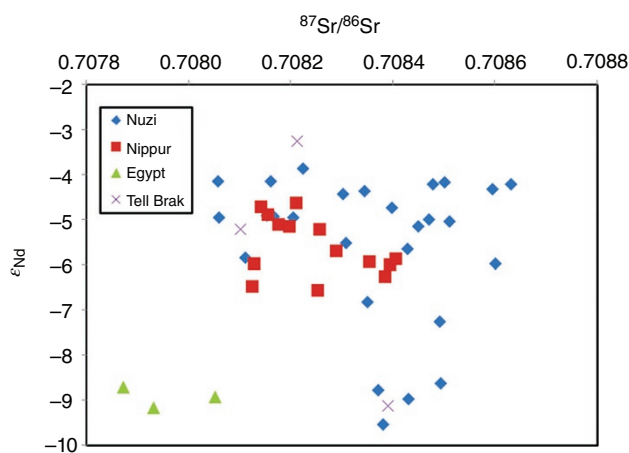


Figure 6 The higher resolution of isotopic analyses: distinguishing glass made in Egypt and in three other places in Mesopotamia from Sr and Nd isotopes of Late Bronze-Age samples [22]. Neodymium isotope ratio of the glass (gl) expressed as $\epsilon_{\text{Nd}} = 10^4 \left[\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{gl}} / \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{ref}} - 1 \right]$ with respect to that of a geochemical reference.

evidence that exchange did take place, e.g. the materials found in the Uluburun shipwreck in the Aegean, East of Rhodes.

6.4 Antimony

Antimony was used as an opacifier in Late Bronze to Iron Age glass. It has been suggested that it was added to the glass batch in the form of an ore (e.g. stibnite, Sb_2S_3) or possibly in its native, metallic form. Despite the fact that many analytical studies have been devoted to antimony as a raw material for colorless glass, compositional analysis had not been able to reveal the provenance of the actual minerals used. Determinations of Sb isotope ratios of ancient glass provide a new means of looking at this source. A first database of possible stibnite ore sources has thus been developed [22]. The Sb isotopic composition of LBA glass does not show a significant difference between Mesopotamian and Egyptian glass, which suggests that all factories in both Mesopotamia and Egypt used similar (or identical) sources. As this antimony has an isotopic composition that significantly differs from that of any stibnite source known from the Mediterranean area, the Near East or eastern Europe, its source is unlikely to be situated there. Likewise, LBA glass is also significantly different in Sb isotopic composition from Roman to early Byzantine glass, for which several Sb sources (as stibnite) seem to have been used and extensive recycling was common.

Although further possible sources in Iran remain unexplored, the only likely origin of the antimony used as the opacifier in ancient glassmaking throughout the Near East lies in the Caucasus where antimony metallurgy developed and native antimony and antimony-rich minerals were specifically mined. Hence, while Sr–Nd isotopic analysis clearly separates glass production in Mesopotamia and Egypt, each region using its own silica and flux sources, the opacifier tells a different story: Sb was used to opacify glass, and factories in Mesopotamia and Egypt seem to have used the same Caucasian source of the material, from the region where also Sb metallurgy first developed. In this way, a link between the development of the metal and glass industries can be shown and exchange or trade in antimony be suggested over long distances.

6.5 Copper and Boron

Because lead is one of the major impurities present in copper, its isotopes are used to distinguish different metal sources, in particular ancient copper alloys (cf. *supra*). However, significant overlap may exist between different ore fields and areas of origin. The application of isotopic analysis of Cu in archaeometry to distinguish different

groups of artifacts and metal sources offers new perspectives, especially in combination with that of Pb. Differences in the Cu isotopic composition between sulphidic and oxidized ore deposits have been reported. They could serve to distinguish the type of ore used in ancient technology, but application to provenancing glass has remained of little use so far [22].

Next to silica as a raw material for glass production, a flux is used to lower the melting temperature of pure quartz. The B isotopic composition of evaporites (like natron) has been used successfully in geological studies to distinguish different environments, and has been used to compare ancient natron flux and glass. Although plant ash glass also contains B in a content an order of magnitude higher than natron glass, this isotopic system has not been explored in provenancing this glass type [23].

7 Perspectives

With the specific information provided especially by elemental and isotopic analyses, archeologists may understand the origin (in some cases, the nature) of the raw materials used in artifact production and can begin to contribute to understand better past trade, (socio-)economic manufacturing conditions, and eventually the ancient economy. Ideally, the interpretation should combine the results with evidence from archeological excavations, historical sources, and typo-chronological study. The main issue in these archeological studies is the fact that the access to analytical facilities may be restricted and/or expensive, especially for isotopic work. More laboratories and research groups investigating isotopes in artifacts should be established, to allow for a broad base of research, enough input of new materials, and new applications of different isotope systems, and in particular new ideas and interlaboratory comparison. In particular, a synergy with the disciplines of chemistry and earth sciences would be effective in this respect, and would facilitate further work in the analysis of ancient glass.

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10.3

Roman Glass

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1 Introduction

Although the first man-made glass vessels emerge in the archeological record in the sixteenth century BCE (Chapter 10.2), for the next 1500 years glass remained a rare and difficult-to-access material, typically opaque and strongly colored. For much of this time, glass was seen as an artificial stone and its use was restricted to the elites of societies in western Asia and the eastern Mediterranean [1]. In the first century BCE, however, a revolution occurred. Technological developments, notably the recognition that hot glass could be inflated with an iron blowpipe, and the melting of raw materials on a scale of tonnes, allowed an expansion of production to supply the demands of the Roman Empire. At its maximum extent, this Empire stretched from Syria to the Atlantic, and Roman glass has been found in archeological contexts as far afield as Japan and Norway.

Scale and technical prowess are two of the defining characteristics of the Roman glass industry. In terms of scale, it has been estimated that a single large public building, the Baths of Caracalla in Rome, required of the order of 300 tonnes of glass window pane and wall mosaic in its construction [2]. In terms of technological achievements, Roman glass was more-or-less equivalent to that of an eighteenth-century European industry, with sophisticated but empirically based methods of manipulating color and form.

In this chapter, I consider the “long” Roman glass industry, where the making of glass raw material was centered on the south-eastern Mediterranean, and based upon the use of naturally occurring sodium minerals and quartz-calcite sand. This tradition of making was

established around the middle centuries of the first millennium BCE and did not finish until around 800 CE, by which time the major centers of glassmaking were no longer Roman but part of Islamic societies. The glass material itself still kept a distinctively Roman character, however.

2 Glass Synthesis

2.1 The Importance of Natron

The only detailed contemporary account of Roman glassmaking is provided by the *Historia Naturalis* of Pliny the Elder, written in about 70 CE. Pliny's account is in many respects vague and open to interpretation but, along with reports of other classical authors such as Strabo (–64 to +25) and Flavius Josephus (30 to ~100), it is clear that it mentions glass made from sand was found close to the mouth of the River Belus (modern R. Na'aman), in the Bay of Haifa. Modern analyses of eastern Mediterranean coastal sand between the Nile and southern Lebanon indicate that it mainly comprises quartz with subordinate shell (CaCO_3) and minor feldspar. With the addition of appropriate amounts of soda, the sands around Haifa would yield a soda-lime-silica glass with a typical Roman composition, containing around 3 wt % Al_2O_3 and 8 wt % CaO (Table 1). Compared with other sands of the coast of Israel, those from the Bay of Haifa have a low color index, implying a relatively low iron content, so that they were likely among the best on the eastern Mediterranean coast for the manufacture of glass. Pliny is also clear that the preferred glassmaking flux was Egyptian *nitrum*, identified as evaporitic salts precipitated from soda lakes in the Wadi Natrun, some 50 km northwest of modern Cairo and from a number of other lakes in the Delta region [3].

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Table 1 Example compositions of natron-based transparent glass of various Roman compositional types.

	Roman-Sb	Roman-Mn	HIMT	Egypt I	Levantine
Century	1st–3rd	1st–3rd	4th–5th	7th	8th
SiO ₂	69.00	69.83	64.49	71.36	73.76
Na ₂ O	19.06	16.05	19.07	17.02	12.10
CaO	6.23	7.72	6.22	3.04	7.42
Al ₂ O ₃	1.71	2.24	2.88	4.20	3.58
K ₂ O	0.39	0.62	0.41	0.53	0.45
MgO	0.40	0.54	1.23	0.81	0.69
Fe ₂ O ₃	0.41	0.42	2.28	1.55	0.61
TiO ₂	0.06	0.07	0.49	0.47	0.12
MnO	0.02	1.14	2.02	0.05	0.02
Sb ₂ O ₅	1.03	—	—	—	—

“HIMT” is a type with particularly “high iron titanium and manganese.”

The most reactive flux in the Wadi Natrun assemblage is the sodium carbonate mineral *trona* [Na₂(CO₃) · NaH(CO₃) · 2H₂O], but mixed salts, sulphates, and chlorides are also abundant. These are collectively termed “natron” by archeologists, although this is strictly incorrect, not only because mineralogically defined natron actually is Na₂CO₃ · 10H₂O, but also because the extent to which the trona was deliberately selected or purified for glass-making is not fully understood. However, it is clear from nineteenth and twentieth-century experience with the manufacture of *saltcake* (sodium sulphate) glass that the presence of minor amounts of charcoal in the batch, inevitable in the wood-fired installations used by the Romans, would have decomposed sodium sulphates to the more reactive sulphites and promoted melting. Unreacted salts would have then separated as an immiscible scum or gall, which could be skimmed from the surface of the molten glass, as actually indicated by the fact that virtually all Roman glass contains of the order of 1 wt % chlorine, which is around its solubility limit in soda-lime-silica melt at high temperature, along with minor amounts of sulphate.

In the widely accepted sand-plus-natron model for glass manufacture, lime [CaO] is generally considered as an incidental component in the sand rather than as an intentional additive to the glass batch. Whereas this is the generally held view, it may not necessarily have always been the case so that some authors consider that lime was added deliberately instead. Pliny himself indicated that shell was added to glass, which might have indicated an attempt to balance the composition by addition of lime. The obvious problem here is that it is difficult to distinguish by compositional analysis intentionally added crushed shell from a shelly component of beach sand.

The relatively pure character of Egyptian natron and the low amounts of accessory minerals in the glassmaking sands yielded glasses with relatively low amounts of potassium and magnesium oxides, typically around 0.5% each. These *low-magnesia* soda-lime-silica glasses are clearly identifiable in the archeological record. Plant ashes, with significantly higher concentrations of MgO and K₂O, were the favored source of flux for most other glassmaking traditions from the Bronze Age through to the Renaissance. Because they gave rise to glasses having typically an excess of 2% each of these components, natron glass is very distinctive. Examples of a range of colorless and transparent glasses are presented in Table 1, where Al₂O₃ in the range 2–3 wt % is characteristic, whereas Fe₂O₃ is invariably present at 0.3 wt % or greater, an order of magnitude higher than the specification for modern colorless glass.

2.2 Melting Furnaces

The sheer size of Roman glass production has raised the question of how the melting process was conducted. Because archeological evidence for large-scale furnaces was lacking, it was commonly assumed that glass was made in the workshops where vessels were shaped. In the 1960s, however, a large slab of failed glass, weighing 8 tonnes and measuring c. 3.4 × 2 × 0.5 m was first reported by Robert Brill from a cave in the Byzantine necropolis at Beth Shearim, Israel. This slab contained excess CaO (16 wt %), which led it to devitrify on cooling to calcium silicate, which presumably led to its abandonment by the glassmakers. For many years it was considered something of an oddity, but in 1992, in Beth Eli'ezer, a location near Hadera, archeologists of the Israel Antiquities Authority reported an array of 17 furnace floors of tank furnaces, each of which would have melted a slab of glass equivalent in size to that at Beth Shearim (Figure 1) [4]. The Beth Eli'ezer furnaces are early Islamic (eighth century) but the products are of Roman-type composition.

More recently, the remains of more Roman tank furnaces, which would have contained between 8 and 20 tonnes of glass, have been excavated in the coastal strip of modern Israel, and in Egypt, close to the sources of good-quality sand and of natron [5]. These rectangular furnaces operated on the reverberatory principle whereby heat from fire boxes at one end of the tank was reflected from an arched roof down onto the surface of the glass. The raw materials were added in layers to facilitate melting, which took place over weeks or more at temperatures that were not especially high relative to those of pottery kilns of the period, probably around 1100 °C [5].

Our understanding of the details of the process and the operation of the furnaces is in need of refinement, but has



Figure 1 Array of excavated floors of tank furnaces at Bet Eli'ezer, near Hadera, Israel. Each furnace is thought to have melted sand and natron to make around 8 tonnes of glass. *Source:* Photo Jochai Rosen, courtesy Israel Antiquities Authority.

been greatly informed by ethnographic investigation of a recently active furnace in India, which melted a slab of around 3 tonnes of glass in a firing that lasted for 30 days [6]. Detailed information on the fuels used is not presently available, but it is assumed that, in the Levant and North Africa, where timber resources were limited, the by-products of agricultural industries producing commodities such as sugar and olive oil would have been used. There appears to be no evidence for the use of charcoal as a fuel. Actually, charcoal would not have been necessary to achieve the required temperatures but, more importantly, the reducing atmospheres generated by this fuel would have produced strong iron-related discoloration of the glasses, which contained over 0.3% Fe_2O_3 , and in some cases up to 3%.

3 Provenance and Location of Glassmaking

The recognition that glass was made as a bulk material in large installations close to the sources of sand and alkali in

the eastern Mediterranean has revolutionized our understanding of Roman glass and of its composition. It is now clear that glass was transported in the form of raw chunks from the *primary* glassmaking facilities to workshops across the Empire where it was fabricated into vessels. There is abundant evidence for the long-distance transport of raw glass in the form of angular chunks or lumps, which have been found in shipwrecks, such as that west of the island of Les Embiez, off Cannes, in the Mediterranean. The raw glass was remelted and shaped in *secondary* workshops into vessels, windows, and small decorative items such as beads, bangles, and amulets for local or regional consumption. This current understanding is summarized in Figure 2.

This model of production division means that the use of chemical compositions to attribute glass vessels to the workshops where they were formed is a challenging endeavor. Considerable attention has nonetheless been paid to the categorization of glass into compositional groups related to the locations of primary production because deciphering the trade of raw glass represents a tool to help understand the ancient economy.

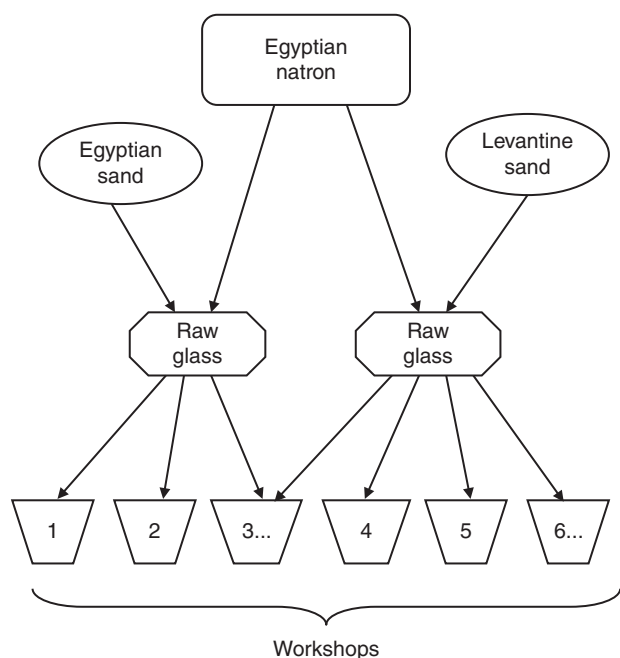


Figure 2 Model for Roman glass production as currently understood. Egyptian soda was transported to primary production centers in Egypt and on the Levantine coast where it was mixed with local sand and melted into glass. The raw glass was transported to numerous workshops around the Empire to be remelted for the production of vessels and windows.

As Roman glass was made from sand and natron, the latter being a relatively pure mixture of sodium salts, the characterization of a glass source essentially reduces to a matter of sand geochemistry. Roman glassmaking sand can be considered to have comprised four constituents: quartz, limestone/shell, feldspar, and heavy minerals. The initial identification of primary production groups has mainly focused upon major and minor elements, where SiO_2 is a proxy for quartz, Al_2O_3 for feldspar and clays, CaO for shell/limestone, and Fe_2O_3 for heavy minerals. Data for these constituents are widely available through major-element analyses performed by different laboratories, which are generally sufficiently compatible to demonstrate relatively subtle differences between the groups (Table 1). It has, for instance, become clear that TiO_2 content is a very effective discriminant between Egyptian and Levantine glass sources, thanks to which it is possible to recognize around nine major groups (Figure 3).

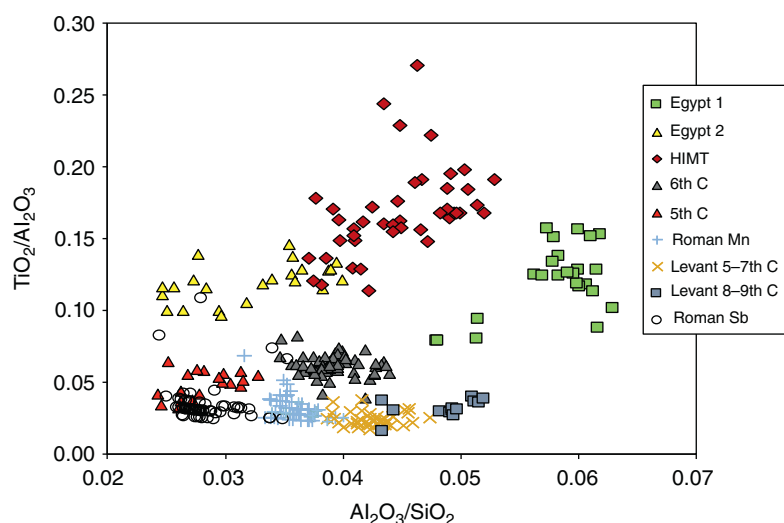
Recently, more detailed information has been drawn from isotopic analyses because variations of the ratios between the abundances of radiogenic and non-radiogenic isotopes may represent a tracer of the source of a given chemical element. In this respect, strontium is especially useful for deciphering the origin of lime

because, as an alkaline earth element, it closely follows Ca in geochemical cycles and, in particular, in the carbonate precipitation of animal shells. Now, ^{87}Sr is the only radiogenic isotope of strontium, forming by radioactive decay of ^{87}Rb , so that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rocks and minerals increase with their geological age as well as with their Rb content. In sea water, strontium originates from the weathering of all types of rocks. Its $^{87}\text{Sr}/^{86}\text{Sr}$ value has also increased through time, being dominated in a relatively recent geological past by the erosion of the Himalayas to reach a characteristically high value of 0.7092. Assuming that most of the Sr in glass is derived from the CaCO_3 component in the batch, one discriminates between beach shell (with the $^{87}\text{Sr}/^{86}\text{Sr}$ value close to 0.7092) and other sources of lime that may have higher or lower values. Among several hundred glasses of the first millennium CE, the overwhelming majority was thus made from shell rather than from limestone, having $^{87}\text{Sr}/^{86}\text{Sr}$ values in the range of 0.7087–0.7092 [10]. This conclusion thus is concordant with the account of Pliny and other classical authors on the use of beach sand to manufacture glass, only the chronologically latest-occurring group shown in Figure 3 (Egypt II, dating eighth to ninth centuries) having been made from inland sand ($^{87}\text{Sr}/^{86}\text{Sr}$ values: 0.7079–0.7081) [10].

Insights into the origin of sand can also be gained from isotopic analyses, but in a somewhat more complicated way through variations of $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. Like the other lanthanides, neodymium is a rare earth primarily present in the heavy-mineral fraction of a sand (Chapter 1.2). Because ^{143}Nd forms by the radioactive decay of ^{147}Sm , the bulk $^{143}\text{Nd}/^{144}\text{Nd}$ of a sand therefore reflects the age of the source rocks that weathered to produce it. In practice, $^{143}\text{Nd}/^{144}\text{Nd}$ is frequently expressed relative to the primordial isotopic composition of the solar system to give a parameter $\mathcal{E}_{\text{Nd}}$, which is largely positive for young volcanic rocks and strongly negative for older crystalline rocks. This relationship is very useful in investigations of Roman glass production because the beach sands of the eastern Mediterranean carry heavy minerals predominantly deposited by the Nile, which were derived from the young volcanic rocks of East Africa.

The $^{143}\text{Nd}/^{144}\text{Nd}$ of a glass can therefore act as a fingerprint for the region of origin of the sand. A survey of the beach sands of the western Mediterranean reveals $\mathcal{E}_{\text{Nd}}$ typically much more negative (typical values –8 to –12) than for the coasts of Palestine and Egypt (typical values –1 to –6). The majority of Roman to early Islamic glass, including that from primary production furnaces on the Levantine coast, has $\mathcal{E}_{\text{Nd}}$ values in the range –3 to –7, consistent with production in the eastern Mediterranean as opposed to the western Mediterranean, where $\mathcal{E}_{\text{Nd}}$ would be significantly lower [10]. Hence, most authors now agree that the majority of natron glass

Figure 3 Main compositional groups of the first millennium CE as determined from differences in major-element contents. Source: Data from [7–9].



was made in the regions of modern Egypt, Israel, and possibly Lebanon.

If neodymium isotopes provide a useful tool to determine the general region of origin of a glass, they are less effective for the determination of a precise origin. The determination of minor and trace elements made possible by the adoption of laser ablation mass spectrometric methods is proving effective in this area. For example, a glass in the natron tradition characterized by high trace contents of boron and lithium has recently been demonstrated to originate from western Anatolia where there are extensive borate deposits [11].

To summarize, it currently appears that most Roman glass was made from sand and mineral alkali in the eastern Mediterranean. Whereas Pliny suggested that glass was produced from its raw materials in Italy, Gaul, and Spain, the isotopic evidence suggests that any production that occurred in these regions was likely minor. Production of a small proportion of glass further West has been suggested from the data [10], but the locations of these productions are not clear.

4 Color Generation and Control

4.1 Transparent Glass

Roman transparent glass of the first to third centuries CE typically contains around 0.4 wt % Fe_xO_y . As revealed by X-ray absorption spectroscopy analyses (Chapter 2.2) of glass vessels and material from production sites [12], around half of this iron is Fe^{2+} whose strong absorption in the red part of the spectrum imparts a distinct green-blue hue to typical transparent glass from primary furnaces (Chapter 6.2). However, a frequent practice was to add manganese dioxide [pyrolusite, MnO_2] or

antimony oxide [Sb_2O_5] to the glass to oxidize the iron and minimize this blue color. Glasses decolorized in this way have over 90% of their iron as Fe^{3+} and are virtually colorless in vessels with walls a few mm thick [12]. Glass decolorized with antimony had the least tint and, as concluded from the limited available data, a higher $\text{Fe}^{3+}/\Sigma\text{Fe}$, presumably because of the relative potential of the $\text{Sb}^{3+} - \text{Sb}^{5+}$ redox couple (Chapter 5.6). The decolorizers were often added to the batch at the primary/raw glassmaking stage, as, for example, indicated by the composition of glasses from the furnaces of the Wadi Natrun.

According to Pliny, colorless glass resembling rock crystal was the most valued type in the later first century CE, which appears to have also been the case around 300 CE, when the Edict of Maximum Prices by the emperor Diocletian (r. 284–350) specified the cost of green-blue glass to be about two-thirds that of colorless glass [13]. Limpid greenish-blue glass is the most common type encountered, whereas Sb-decolorized glass was more frequently used for high-quality vessels than Mn-decolorized glass, for example, those with cut decoration where optical quality was most important. It may be that the effectiveness of Sb as a refining agent was also a contributor to the value attached to this type of glass.

From the fourth century, marked changes occurred in the glass industry. New production centers used sand that often contained in excess of 1% Fe_2O_3 so that the quality of much of the glass declined. Whereas the intensity of the color appears to have been reduced by MnO_2 addition, the higher total iron typically resulted in a yellowish green tint even when the bulk of the iron was oxidized. In some compositional groups, there is a general correlation between iron and manganese contents, which appears to indicate a systematic approach to control color; similar correlations are not seen again until Renaissance Venice (Chapter 10.7).

4.2 Colored and Opaque Glass

For production of colored glass, the Roman technologies were closely similar to those used since the second millennium BCE. For translucent glass, the color was determined by a limited range of elements – Co^{2+} (deep blue); Cu^{2+} to give turquoise, or modified by lead or iron to give green; Mn^{3+} to give purple. Amber, due to the ferri-sulphide chromophore (S^{2-} – Fe^{3+} charge transfer, see Chapter 6.2), was formed under exceptionally reducing conditions in the primary glassmaking furnaces. Copper is typically associated with minor amounts of tin, lead, or zinc and is therefore believed to have been added in the form of the oxide scale formed upon heating of scrap bronze; the locations of the ores that provided the cobalt and manganese are not yet identified.

Opaque and strongly colored glass was also routinely made with a variety of appropriate compounds [14] (Figure 4, Table 2). High-quality opaque white glass, for instance, resulted from precipitation of calcium

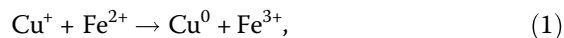


Figure 4 The Lycurgus Cup (fourth c. CE) depicting the myth of King Lycurgus in cut openwork. The cup is colored by Ag–Au–Cu nanoparticles and appears red in transmission and green in reflection. It was cut from a thick-walled blown blank. The metal base and rim were added in early modern times. Height: 16.5 cm (with metal mounts). Source: British Museum 1958, 1202, © The Trustees of the British Museum.

Table 2 Example compositions of Roman opacified glass.

	Blue	White	Yellow	Green	Dull red	Bright red
SiO_2	64.19	67.47	65.34	65.57	56.83	42.80
Na_2O	15.46	15.12	16.59	17.43	12.47	10.52
CaO	6.97	6.46	5.74	6.18	8.10	4.77
Al_2O_3	1.99	2.30	2.08	1.99	2.11	1.55
K_2O	0.62	0.62	0.57	0.67	2.05	0.48
MgO	0.57	0.89	0.56	0.73	2.14	0.51
Fe_2O_3	1.01	0.48	0.84	0.77	1.72	0.36
MnO	0.85	0.40	0.25	0.39	0.32	0.41
Sb_2O_3	4.46	4.35	0.72	0.57	0.32	1.43
PbO	2.26	0.31	4.55	2.75	10.05	27.10
CuO	0.27	0.05	0.04	1.46	1.91	9.20
CoO	0.25	—	—	—	—	—
Crystals	Ca–Sb	Ca–Sb	Pb–Sb	Pb–Sb	Cu	Cu_2O

antimonates [$\text{Ca}_2\text{Sb}_2\text{O}_7$ and CaSb_2O_6] upon addition of antimony. In combination with Co^{2+} and Cu^{2+} dissolved in the glass matrix, these antimonates could alternatively produce deep opaque blue and turquoise, respectively. Another ingredient was lead antimonate [$\text{Pb}_2\text{Sb}_2\text{O}_7$]. It was preformed as a pigment before mixing with the soda-lime-silica glass in which its distribution was less homogeneous. It was relatively unstable at high temperature but yielded opaque yellows and greens along with dissolved Cu^{2+} . As for opaque reds, they were produced by the precipitation of metallic copper particles of the order of several hundred micrometers diameter. The reduction of the dissolved copper oxide into metal according to the reaction



was achieved by addition to the molten glass of either iron or of carbon in the form of furnace ash. Another type of red glass was produced by the precipitation of dendritic cuprous oxide [Cu_2O , cuprite] in a lead-rich soda-lime-silica glass matrix; a purer *sealing wax red* was in general obtained than with metallic particles, which yielded a more red-brown hue (Table 2).

As a translucent material, red glass was extremely rare before the modern period but a small group of vessels dating to the fourth century owe this color to metallic alloy nanoparticles (Chapter 6.2). The most famous is the Lycurgus Cup of the British Museum (Figure 4), which contains 30 wt % Au, 60% Ag, and 10% Cu [15]. Because the cup appears red in transmission and green in reflection, the suggestion has been made that it symbolizes the

ripening of the grape. How gold was dissolved in the glass by the Romans is uncertain, but it is usually accompanied by silver and copper in very variable amounts, perhaps pointing to a poorly controlled reaction between hot glass and molten metal such that the most easily oxidized constituents of a gold alloy (Ag and Cu) were dissolved disproportionately.

Recent work on pink or flesh-colored tesserae from mosaics, again mainly dated to the fourth century, indicates that they owe their color to a combination of gold nanoparticles and calcium antimonate [16]. It therefore seems that gold coloration was a deliberate technology adopted by the Romans at this time. Significant amounts of tin are not present in these glasses. It appears that the reduction of Au^+ to Au^0 was achieved instead by the donation of an electron from Sb^{3+} or Fe^{2+} .

At some time in the fourth century, the use of antimony as a glass additive appears to have ceased or greatly diminished. Since Sb-decolorized glass was no longer made, the occurrence of antimony-opacified glass in some enamels and mosaics may be explained in terms of recycling or reuse of old colored glass. Whereas manganese became the only decolorizer used, opacification was achieved largely with compounds of tin, specifically SnO_2 (white) or $\text{Pb}_2\text{Sn}_2\text{O}_6$ (yellow). Presumably because tin then became either inaccessible or too expensive, by the tenth century, crushed quartz was widely used to opacify the tesserae of Byzantine mosaics.

A currently unsolved problem is that of the places where glass was opacified and colored. Colored and opaque glass was much less common than weakly tinted glass, more costly to produce, and used particularly in elite houses and institutions, for example in wall mosaics. Furthermore, archeological finds of certain strongly colored glass such as cameo vessels are concentrated in or around Rome. Hence, it is commonly assumed that the production of opaque glasses was concentrated in major centers, which is why Rome and Alexandria are generally thought to have been important production centers for high-value or “luxury” glass.

5 Secondary Production and Consumption

5.1 The Blowing Revolution

Colorless and weakly colored green-blue blown tablewares – jugs, bowls, cups, flasks, and plates – are the most visible products of the Roman glass industry in museum collections (Figure 6). As broken fragments, they are indeed the most commonly retrieved type of glass from archeological excavations. Their widespread appearance in the first century CE represented a revolution in

production made possible by the introduction of inflation with a blowpipe, coupled with a substantial increase in the manufacture of raw glass from sand and alkali.

Before the middle of the first century BCE, the main methods for making glass vessels were limited to winding around a core, or slumping a disc of hot glass over a typically hemispherical or conical former to produce a bowl (Chapter 10.5). Open forms made by the latter method are the major component of Hellenistic and early Roman assemblages of glass. The use of polychrome canes in conjunction with this technique allowed the production of *mosaic* glass vessels – bright multicolored bowls demonstrating a wide and highly imaginative range of decoration, which implied great skill in both conceptualization and design and in its implementation (Figure 5).

The free manipulation of hot glass made possible by blowing allowed a far greater range of forms to be produced, including vessels with narrow openings (Figure 6). Blowing was fast and did not require the preparation of molds or formers and the removal of their traces when the vessel had been shaped. As there was no core material adhering to the interior, it was more favorable to the use of relatively inexpensive transparent and uncolored glass. It allowed the manufacture of vessels with much thinner walls, hence required less glass. Therefore, it resulted in an upscaling of production so that glassware became widely available to people of relatively modest means. Furthermore, it made possible the blowing of vessels into molds



Figure 5 Mosaic-footed glass bowl, Victoria and Albert Museum 969–1868. Made by first producing a polychrome disc from colored glass strips and then slumping this over a hemispherical former. Late first century BCE or early first century CE. Height: 11.5 cm. Source: Copyright Victoria and Albert Museum.



Figure 6 A range of forms displayed by a selected group of blown Roman-glass vessels from burials at Castra, Mount Carmell (Israel).
Source: Photo Mariana Salzburger, courtesy Israel Antiquities Authority.

of stone, ceramic, or metal, and the mass production of cylindrical and prismatic bottles for the transport and sale of liquid goods.

The invention of the blowing technique is not well understood. However, an archeological assemblage of about the right date comprises a dump of discarded and waste glass from a workshop in Jerusalem (cf. Chapter 10.5). Here, glassworkers appear to have been inflating small glass vessels by sealing the ends of folded tubes of glass and blowing the glass tubes [17]. This evocative group of material is very suggestive of the first step toward the practice of blowing glass with an iron blowpipe, but corroborative evidence and a firmer timeline are required. Whereas only a few iron blowpipes have been retrieved from Roman contexts, the glass rings remaining around the blowpipe when glass was blown, known as *moils*, are relatively common, and can include flakes of iron oxide, confirming that blowpipes were typically made of iron or steel.

5.2 Local Workshops

Most large centers of population seem to have had active glass workshops at some point but it is not always clear if these were permanent, long-term establishments or if their operation was short term and sporadic. In Britain,

for example, it appears that even in a major provincial center such as *Londinium*, glass workshops operated sporadically and glass workers were peripatetic, bringing their raw material and establishing a furnace until the fresh glass was exhausted and no more scrap glass could be obtained for recycling from the local population [18]. However, Britain was a province on the edge of the Empire and about as far away from the sources of raw glass as possible, so that permanent workshops are likely to have been a feature of regions more central or closer to the sources of glass.

Furnaces for glass working varied in both shape and size [19]. Crucibles or melting pots are relatively uncommon in the first to fourth centuries. Most furnaces at the height of the Roman Empire melted the glass in a tank, in some cases heated on the reverberatory principle. Understanding of the furnaces is limited at present as typically only their bases are preserved. Designs appear to have varied, with a circular or rectangular plan and dimensions typically less than 1 m in internal diameter. The typical fuel is likely to have been wood, where available, but agricultural by-products such as those of olive-oil extraction as well as animal dung are likely to have been used in more arid regions. For example, excavation of a workshop at Beth Shean in Israel yielded vessels covered in charred olive pits, presumably for annealing (Chapter 10.5).

5.3 Decorative Artifacts

In addition to plain or mold-blown tablewares, a range of other products were available to the Roman consumer [20]. During high-temperature work, trails or blobs of colored or colorless glass could be added to embellish the vessel. Colorless vessels could be cut or engraved, with a stone wheel or, for fine work, a rotating copper wheel with a slurry of abrasive such as quartz or emery. Diamond engraving tools were known in the time of Pliny, but it is not clear how widely they were used. Cameo glass, such as the Portland Vase, where an outer layer of glass has been cut away to reveal an underlying glass of a different color, date mainly from the late first century BCE to the early first century CE. The most sophisticated examples of glass-cutting are the *diatreta* or cage-cups of the fourth century (Chapter 10.5), of which the Lycurgus Cup (Figure 4) is an unusual example with figurative, as opposed to geometric decoration.

A small class of vessels were enameled – painted with powdered opaque glass, which was then fused to the surface (Chapter 10.6). Enameling represented a challenge in that the softening temperatures of the glass paints were frequently similar to those of the underlying vessel so that the operation was carried out by insertion of the painted vessel into the mouth of the furnace for a very short period [1]. Dating to the fourth century, another small group of artifacts is well represented in museum collections. It comprises round vessel bases with designs in gold leaf sandwiched between two layers of glass (Chapter 10.5).

With the widespread adoption of blowing, there was a marked decline in the production of strongly colored glass vessels around the middle of the first century CE. The use of strongly colored glass is then seen in the production of glass tesserae for wall mosaics. These decorated the houses of the wealthy who could sustain the more expensive raw materials and production costs of opaque glass. The tesserae appear to have been cracked off from pizza-like “cakes” of glass, typically around 8 mm thick. Colored glass was also used for beads and for minor decorative elements on certain classes of colorless vessels.

5.4 Windows and Mirrors

Glass windows were widely used to light bath houses and other public buildings while providing heat insulation. Window panes were frequently made by the *casting* process whereby the molten glass was poured onto a flat surface, pressed flat, and then manipulated into a rectangular shape by reheating and pulling with tongs. Production of windows through reheating and opening up a blown cylinder of glass (Chapter 10.8) seems to have become more common in the fourth century [21].

To make mirror glass, a large glass bubble was inflated and poured in molten lead to coat the inside. The resulting mirrors were made from trimmed fragments broken from the bubble that were set on plaster or wooden frames. They are rarely, if ever, more than a few centimeters across. A number of plano-convex transparent lens-like objects have been reported but their function is unclear. They have limited magnifying power (c. $\times 4$) and might have been used as decorative inlays in furniture or architecture. Whereas it is possible that occasional items were made to specification for technical purposes, we have no archeological evidence that there was any routine production of scientific or technical glassware. There are plenty of glass phials, which could have held medicines but also oils and perfumes, so they are not really strictly scientific or technical; some described as Roman and potentially alchemical seem to be in fact Islamic in date. Indeed, at present we have no evidence of the manipulation of glass composition for any other purpose than the modification of color or the cost and availability of raw materials.

6 Recycling, Shifts in Production, and Decline

Recycling of glass was common practice throughout the period [22]. Contemporary literary evidence indicates that scrap glass was exchanged for sulfur matches on the streets of Rome. Caches of old and broken glass have even been discovered by archeologists. A striking evidence for recycling is the barrel of scrap glass recovered from the third-century wreck of the *Iulia Felix* in the Adriatic [8].

At its height in the first to third centuries, Roman glassware was produced in two compositional categories – an antimony-decolorized glass with around 5% CaO and 2% Al_2O_3 and a manganese-decolorized variety with around 7.5% CaO and 2.7% Al_2O_3 . These are distinctive in many ways (Figure 3) and represent two primary production centers. Simple graphical analysis indicates that most glass of this period comprises one of these types or more frequently a mixture of the two, owing to the extensive practice of recycling at this time (Figure 7).

Following the apparently abrupt end of decolorization with antimony in the fourth century, a new greenish glass, richer in iron ($>1\%$ FeO), became dominant over much of the Roman world. It is thought to have been made in Egypt and was used alongside a continuation of the Mn-decolorized glass made on the Levantine coast. Over the next few centuries, a series of relatively abrupt changes in the composition of natron glass indicates shifts in the location of production within the South-East

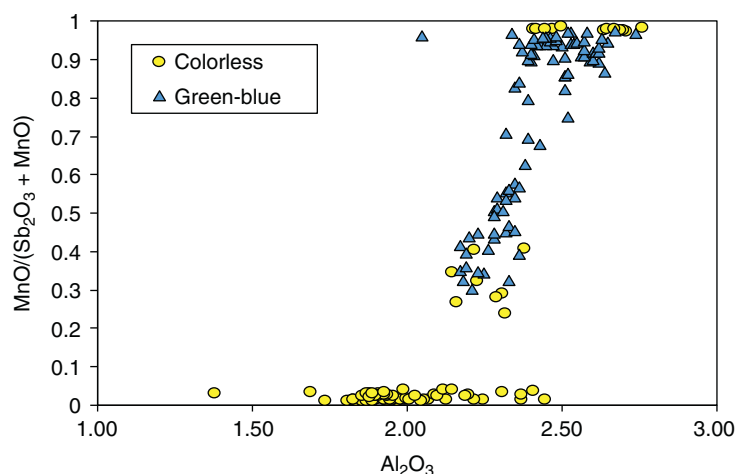


Figure 7 Typical mixing line between Roman antimony-decolorized glass, with low Al_2O_3 , and manganese-decolorized glass, with high Al_2O_3 [22], displayed by Roman glass fragments from the Iulia Felix wreck in the Adriatic [8].

Mediterranean region (Figure 1). Over the same period, there is a gradual decline in the quality of glass made in the Levant, where the use of manganese decolorant diminished and the average soda content of the glass reduced until, in the eighth century, a bluish glass with around 12% Na_2O and 75% SiO_2 became the characteristic product (Table 1). This period of decline corresponds to the contraction of the Roman Empire and a dramatic reduction in the volume of Mediterranean trade. Indeed in the post-Roman (early medieval) societies of Europe, fresh glass from the Southeast became increasingly difficult to obtain. From Italy through to Britain, evidence of a dependence upon recycled glass becomes increasingly apparent from the end of the sixth century.

An important source of this recycled material may have been the wall mosaic and window glass of the large public buildings, which were abandoned with the decline and withdrawal of Roman administration. Mosaic tesserae were important sources of material for color as well as for raw glass; for example, cobalt-blue tesserae were mixed with colorless glass to produce translucent blue sheets for windows through to the twelfth century. Limpid blue- or green-tinted transparent glass of the eighth–ninth centuries may contain copper, antimony, and lead at high levels, which could have resulted only from extensive recycling of first–third century opaque tesserae, excluding cobalt blues, which were reserved as a source of blue pigment [22].

In western Europe, much of this recycled material was likely imported from the old Roman regions in the South. By the ninth century, it could no longer satisfy the demand for glass, which included the requirements of the growing Christian churches and monasteries. A new formulation was thus developed such that glass began to be made from local sand and potassium-rich wood ash, laying the foundations for the stained glass window industry of the high medieval period (Chapter 10.8). In the Islamic East,

natron-based glass production declined in the ninth century when the natron flux was replaced by soda-rich ash, produced by burning halophytic plants from desert and coastal environments, marking an end to the Roman tradition of glassmaking.

Although current opinion is that glass was no longer made from Egyptian natron after around 900 CE, natron-based glass continued to be in use through the thirteenth century for some purposes. The compositions of glass enamels on Romanesque copper-alloy reliquaries and plaques of the twelfth century correspond precisely to the opaque glasses of the second–third centuries. Writing around 1120 CE, the monk Theophilus tells us that these were obtained from the old buildings of the pagans (Romans) [23]. He also indicated that window glass was colored blue by mixing blue tesserae with contemporary wood ash glass. Analysis of medieval church windows supports this account [22].

7 Perspectives

The preservation of ancient cultures is tenuous. Analytical samples of heritage materials such as glass can be difficult to obtain, which is why the available data have been collected in a somewhat opportunistic and arbitrary fashion. For some regions they depend upon museum material that may date back to the early twentieth century or before. Even so, over the past 20 years, new archeological discoveries and improvements in the understanding of vessel chronology, along with a marked expansion in scientific investigations, have led to the development of a consistent model of Roman glass production.

Detailed archeological studies focused on glass assemblages at specific sites, on shipwrecks, or on the geographical distributions of specific types of glass objects are

continually enlightening our understanding of the ways in which glass was perceived, valued, used, and reused. New trace element and isotopic approaches are likely to be applied to shed light on the sources of fluxes, colorants, and opacifiers. Although several primary production sites have been identified, those of some of the major types of glass remain to be discovered whereas the possibility of primary production in the West requires more attention. Modeling and experiment offer the potential to understand better furnace operation. In this respect, the determination of oxidation states in experimental glasses could allow furnace conditions to be determined.

Alongside other evidence, this framework will allow glass to be used to yield important information on industry, trade, and the ancient economy. The wider reasons behind technological innovation and change, the movement of production locations, and the growth and decline in glass use will be amenable to investigation as our understanding of chronology and regional variation becomes more refined. In this way, the study of glass will bring new and valuable information on the inner workings and evolution of the Roman Empire itself.

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10.4

Glass and the Philosophy of Matter in Antiquity

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1 Introduction

In Antiquity, glass, more than any other product made out of earthly materials, could be easily shaped and colored to imitate precious stones or mineral substances. Egyptian priests projected a religious meaning onto the mineral kingdom, such that each mineral was endowed with special properties that evoked the presence of the gods [1]. When it was discovered that glass could imitate lapis lazuli, Egyptian craftsmen began to reflect upon the properties of matter and the value that should be attributed to imitations. Were these mere counterfeits or faithful replicas of the natural stones? This was a critical question because, with the XVIIIth dynasty (c. 1543–1292 BCE), the production and trade of both artificial and natural lapis lazuli became an important aspect of Egyptian culture and religious rituals.

The Egyptian glassmaking tradition survived in Hellenistic Alexandria, exporting both technical know-how and theoretical insights to Palestine and, during the Roman Empire, along the Mediterranean coastline. Attention to archeological data in particular reveals that Egypt played an exceptionally important role in directing the interest of early Greek philosophers and naturalists on the properties of glass.

Of particular importance in this respect was the philosophy of matter first expounded by Empedocles of Agrigento (483–424) according to which everything in the sublunar world (the Earth and its atmosphere) was made up of various proportions of the four elements, fire, air, water, and earth. When Plato (c. 428–347) and his former disciple

Aristotle (384–322) subsequently went one step further with their own explanations for the transformations undergone by these elements, their theories had an obvious bearing on glass, whose marvelous properties such as natural luster and transparency required a rational account in terms of the action of fire upon a variety of earthly substances. And not only was glass representing the dramatic transformation of insignificant raw materials into a remarkable substance akin to gems, but it also had many common features with metals in general. Hence, glass became closely involved in alchemy when metal transmutation became an important goal of this *Sacred Art*, and such efforts could only increase after the technical revolution triggered by the invention of glassblowing during the first century BCE.

Before examining glass within the context of ancient philosophy of matter, however, we will have to go back in time and consider how this material was originally considered in Mesopotamia and in Egypt. From Empedocles' to Plato's and Aristotle's theories, we will then briefly present the basic relevant concepts before delving into the mutual relationships of glass and alchemy. Finally, the role played by Byzantium in the transmission of the alchemical tradition will be summarized.

2 Near Eastern Views on Glass

2.1 Mesopotamia

From about the twelfth century BCE, Mesopotamian glass and medical texts bore a resemblance in their literary form: they prescribed instructions in the form of recipes, and some even recommended religious rituals and prayers, invoking the need to perform certain experiments during propitious days ([2], Chapter 10.11).

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According to these early Mesopotamian recipes, the chemical operations required to produce colored glass were preceded with a ritual including the worship of images and a libation offering; when the glass was placed into the kiln, a sheep was sacrificed before images of the Gods. Such rites were important because their association with a holy discipline such as medicine underlines the scientific and literary dignity of glassmaking. One of the most important achievements of Mesopotamian glassmaking was the imitation of lapis lazuli. Given the importance of these gems in near-Eastern art and culture, the ability to produce notable quantities of artificial stone represented an important technological advance, although glass was still valued as highly as gold.

Another feature revealed by Mesopotamian texts, which would have important consequences for the history of glassmaking, was the definition of glass itself: the term *bašlu abnu* (molten stone), which announced the Greek *lithos chytè* (molten stone), eventually used by Herodotus (c. 484–420) [3] and other Greek authors. The reference to the chemical operation of melting is significant because the fusing property of glass was shared by other mineral substances, especially metals. In this respect, it seems that at a very early stage glass was not seen as an entirely artificial product but as a natural stone which, like metals, could be fused and modified.

2.2 Egypt

Although the influence of Mesopotamian glassmaking on Egyptian craftsmen is now generally acknowledged, the priority disputes over the invention of this material have overshadowed the different approaches and technologies developed within the two civilizations. In fact, Egyptian craftsmen displayed an extended knowledge of primary ingredients, developed advanced metallurgical techniques that led them to produce a richer variety of colors, and, last but not least, manifested a theoretical interest in the classification of glass within a *philosophy of matter* apparently absent from Mesopotamian texts.

The glass industry made its appearance in Egypt from 1400 BCE during the reign of Akhenaten (r. c. 1354–1338). Like in Mesopotamia, the invention of glass probably derived from the crafts of faience and glaze. These materials consisted of the same ingredients – silica, alkali oxides, and lime in modern parlance – but their technical treatment was completely different, thus resulting in many different vitreous bodies. Both glass and faience were treated as artificial precious stones, however, and Egyptian craftsmen seem to have mastered both techniques with the greatest dexterity.

At least between 1400 and 1050 BCE, glass was of great importance in Egyptian culture for the production of

amulets, beads, vessels, inlays, and the imitation of precious stones. Probably because glass could imitate so many materials, the Egyptians did not coin a specific name to denote it until the third century CE, when the demotic *yl* was used for the first time in the magical papyrus of London [4].

Egyptian craftsmen, like their Mesopotamian counterparts, also defined glass as a “molten stone” or “molten precious stone” (*aA.t-wdH*). Going farther than their predecessors, however, they included glass artifacts within a comprehensive classification of metals and mineral products without finding it necessary to establish a clear-cut distinction between glass and faience, on the one hand, and glazing mineral stones on the other. One definition of glass appropriated the term faience, *THn.t*, which was derived from the verb *THn*: to sparkle, to scintillate, the lightning flash. As the etymology would have been equally effective to denote colored glass, the term later became synonymous with this new artifact.

While sharing the same property of being meltable, substances such as gold and lapis lazuli differed essentially by their qualities of color and brilliance. According to Hecataeus of Abdera (late fourth century BCE), a Greek skeptic philosopher who wrote a book now lost on the history of Egypt, Egyptians believed in a principle of matter which, divided into four elements, became the basis of all living beings [5]. The relation between these elements and the importance attributed by Egyptians to colors in order to classify the products of the mixtures of the four elements would eventually find an important echo in the Greek philosophy of matter.

Because the gods’ influence over the mineral kingdom was so pervasive, craftsmen who were engaged in the manipulation of metals and stones were in touch with godly particles and fluids, and their capacity to transform matter thus placed them in the position of demiurges (Figure 1). It is not without significance that there was no term denoting glassmakers in Mesopotamia whereas in Egypt *irw hsb* denoted the craft of “makers of (artificial) lapis lazuli,” thus showing the professionalization of a skill that would enjoy significant importance within Egyptian society and culture. As a matter of fact, craftsmen enjoyed a higher social status in Egypt than in Classical Graeco-Roman economic contexts. In Egypt, claimed the Greek physician Galen (c. 129–216), new artisanal discoveries were always submitted to the approval of scholars, who provided public notice of the new inventions through inscriptions fixed on sanctuary columns. It was the tradition of omitting inventors’ names from these inscriptions, which, according to Galen [6], caused a multitude of anonymous writings on occult sciences to be attributed to the god Hermes Trismegistus, the founder of all wisdom.

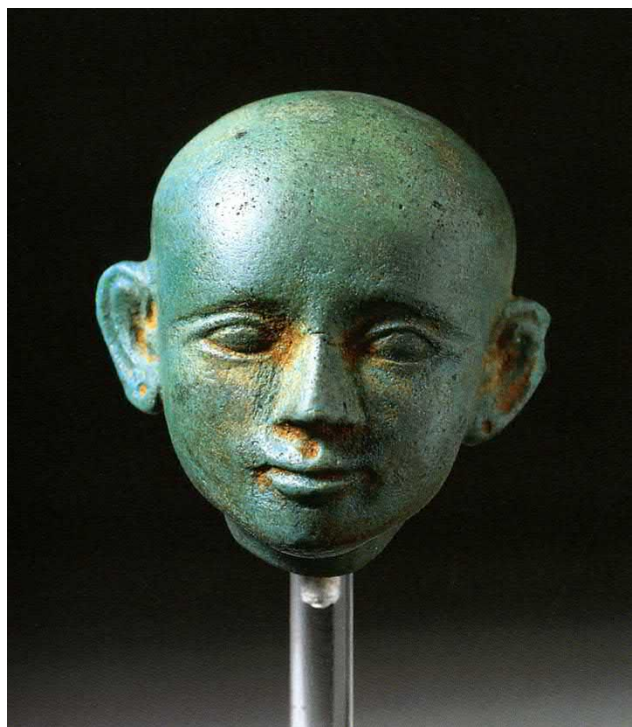


Figure 1 Head of an Egyptian priest made of vitreous material (c. seventh century BCE) from the former Ernesto Wolf Collection. Source: Photo courtesy E.M. Stern.

3 The Glass of the Greek Philosophers

3.1 From Empedocles to Plato

Even though scholars long raised doubts concerning how much was actually known in archaic Greece about glass, today it is clear that techniques had then been imported from Egypt to imitate ceramics and were already used widely. Homer's works, which are often used to show the absence of references to glass in the eighth century BCE, in reality contain many references to a substance called *kyanos* designating a blue glass paste used to decorate temples [7] and warriors' armor. In other passages of Homer and in Philostratus [8] and Aristotle after him, the term *kyanos* is used as an adjective designating the blue, iridescent color of stones, animals, and objects. In another sense *kyanos* designated an actual stone – a natural product that Pliny the Elder (23–79) identified in his *Natural history* [9a] with a blue pigment (*caeruleum*) and by his modern commentators as azurite – a blue stone similar to lapis lazuli.

The Greeks identified metals with products of mineral extraction that were meltable. These included not only real metals such as gold, silver, and copper but also composite bodies, such as glass and some mineral pigments, which were not discernible within ancient philosophies of

matter and would be today designated as metallic substances. What curiously associated these materials was solely their properties of being products of mineral extraction and, above all, of being meltable materials that could change form if submitted to the action of fire through metallurgical techniques.

As already noted, the most influential philosophy of matter in Antiquity was that of Empedocles. Probably the now lost treatise on metals occupied an important place in his poem *On Nature*. But the important point is that, from the advent of this theory, it became necessary to give an empirical foundation to the macroscopic changes visible in a material. On the assumptions that all bodies release effluences and at the same time have pores capable of absorbing other effluences commensurable with them, Empedocles understood that metals “like all other bodies possess a structure” [10] so that the differences among the elements and the compounds were due to the different configurations of their aggregate of particles.

Empedocles' theory of pores was taken up again by his pupil, Gorgias (c. 483–376 BCE) in order to explain the property common to bronze, silver, and glass of forming mirrors capable of concentrating sunlight and acting as burning mirrors [11]. By the way, we must note that, contrary to what is still often believed, the Greeks did make glass mirrors and were well aware of the differing reflecting properties of metals. To establish a distinction of this kind, it was in fact necessary to be much more familiar with the workings of glass and metals than attested to by fragmentary archeological proofs and, above all, by late Latin texts.

Empedocles' philosophical intuition on the structure of matter, based at least in part on his knowledge of metallurgical techniques, received further and more profound consideration by Plato. In his dialogue *Statesman* [12], no distinction was made between “gold and silver, and everything that is mined,” showing the connection between the identification of metals with the technique of their extraction. Metals were substances extracted from the Earth, which, when subjected to the action of fire, were behaving in the same way. Regarding glass, it is interesting to note that one of the first occurrences of the term *hyalos* in the explicit context of natural philosophy is found in Plato's *Timaeus* [13a], his great cosmological dialogue.

This introduction of the term *hyalos* in the fifth century BCE brought with it a more precise understanding of glass. According to some philologists, the substantive *hyalos* derived from the verb *heyin* (to rain), signifying water droplet, whereas others say that it derives from *hals* (salt): the former term exalts the physical characteristics of glass – particularly its brightness and transparency – whereas the latter alludes to its chemical constitution. Whatever

the correct explanation is, in both cases physics and technology were at the basis of the Greek definition of glass.

As for the elements, Plato explained in *Timaeus* that the triangle was their building block so that the four of them represented the four fundamental regular polyhedra, namely, the tetrahedron (fire), cube (earth), octahedron (air), and icosahedron (water) [13b]. In terms of a balanced reaction, the vaporization of water upon heating was, for instance, seen as the rearrangement of the 20 equilateral triangles of one water icosahedron into the 4 triangles of one fire tetrahedron and the 16 triangles of two water octahedra [13c].

In *Timaeus*, Plato could then discuss the interplay of fire and water in metals and define glass [13d] as a mixture of water particles (in a larger proportion) and of earth, which, when subjected to the action of the particles of fire reached the molten state. It is fusibility, therefore, which Plato also attributed to metals, that defined the material character of glass. This concept represented a fundamental step forward in antique metallurgy and eventually also involved a better understanding of what glass was.

3.2 Aristotle

Although paying careful attention to empirical research, Aristotle's primary interest, without doubt, was to construct a coherent philosophy of matter capable of overcoming the limits encountered by that of Plato. This is what he did in the in the fourth book of his *Meteorology* where attention was duly paid to metals, in general, and to glass, in particular. Without falling into the wild speculations of earlier thinkers, Aristotle rejected Plato's geometrical approach to posit instead that the elements should rather be accounted for in terms of four fundamental *qualities*, namely hot, cold, dry, and humid. Fire was then dry and hot, air dry and cold, water cold and humid, and earth dry and cold so that all transformations within the sublunar world was taking place through exchanges of these four qualities.

On this basis, Aristotle proposed elaborate interpretations for the cause of the chemical changes to which matter was subjected. He took his cues from widespread practical and craftsmanly activities such as that of the art of the potter, when speaking of the properties of clay, or the treatment of oil, when describing differences in the solubility of liquids. Likewise, the properties of solid bodies were sifted through a system of categories derived from arts and techniques. In this way, Aristotle proposed to distinguish bodies according to a comprehensive property flow-chart: "to be apt or inapt to solidify, melt, be softened by heat, be softened by water, bend, break, be fragmented, impressed, moulded, squeezed; to be tractile or non-tractile, malleable or non-malleable, to be fissile

or non-fissile, apt or inapt to be cut; to be viscous or friable, compressible or incompressible, combustible or incombustible, to be apt or inapt to give off fumes" [14a].

Aristotle then imagined that the formation of metals and many other mineral bodies were due to the two types of exhalations generated by the Sun's heat: the first liberated watery vapor, which constituted water and insinuated itself into the bodies of which it was a component; the second was dry and very inflammable, deriving directly from the earth. Not limiting himself to characterize metals as meltable bodies extracted from mines, as Plato did, Aristotle also sought to find out the cause of their meltability. He assigned it to the vaporous or watery exhalation, which, thanks to its intrinsic humidity, rendered these bodies susceptible to melting and thereby to reaching the liquid state. Further, the different degrees of fusibility of various metals were, according to Aristotle, due to different proportions of the two basic elements, water and earth, since "all determinate bodies in our world involve earth and water. Every body shows the quality of that element which predominates in it" [14b]. And it appeared that the aqueous element often seemed to prevail: "gold, then, and silver and copper and tin and lead and glass and many nameless stones are of water; for they are all melted by heat" [14c].

In light of Aristotle's classification, one could think that the idea of defining glass as *hyalos*, deriving from the verb *to rain* was not altogether extraneous from the chemical property of this material to reach a molten state at high temperatures. The possibility of producing transparent glass was conditioned by the availability of furnaces capable of reaching temperatures above 1000 °C. Therefore, the substitution in the fourth century BCE of the terms *kyanos* and *lithos chytê* for *hyalos* might have reflected an awareness of technological progress achieved especially in the art of glassmaking.

From this definition, it clearly appears that the Ancients considered the philosophy of matter as distinct from manipulative procedures, thereby allowing them to recognize constitutive differences between various classes of minerals. In fact, in the majority of citations assembled here, it was technique that rendered possible the general definition of a specific class of minerals.

4 Glass and Alchemy

4.1 Art as Imitating Nature

References to glass are found not only in philosophical texts, but in far greater measure in alchemical practices that were half way between philosophical speculation and empirical experimentation. Ancient alchemy played a central role primarily because it was inherent to the



Figure 2 Oil lamp with the illustration of an artisan blowing glass in a pipe. At the center, a glass furnace; on the left, another worker is holding the finished product. First century CE. Source: Courtesy Museo del Belriguardo, inv. 52196, Ferrara.

techniques and knowledge that were essential to the production of glass (Figure 2). The construction and development of furnaces capable of reaching ever higher temperatures, the acquired skill of combining an ever-increasing number of ingredients, the chemical techniques of coloration just as those for counterfeiting gems and precious stones were all aspects shared by craftsmen and alchemists alike [15, 16].

It is difficult, and perhaps historically improper, to try to relate the production of glass by artisans to an attempt at providing metallurgical production with a theoretical and philosophical framework that would have been completely extraneous to practical needs. It is nonetheless odd that historians of glass have neglected alchemical sources by concentrating exclusively on archeological remains and on those texts, by Pliny the Elder in the lead, that have little technical content and, above all, do not reflect the actually widespread knowledge of this material in the ancient world.

If the procedures of the Greek alchemists mostly derived from the technical tradition of Egyptian artisans,

they also depended upon philosophies of matter which, from the pre-Socratics onward, had tried to give rational explanations to the changes wrought upon matter by the action of fire. In most of the alchemical texts of late Antiquity, this is why we find among the authorities and founders of the alchemy the names of Thales, Pythagoras, Democritus, Plato, and Aristotle mixed with those of Egyptian sages.

There is another profound reason why the development of Greek alchemy, which flowered in the Alexandrine epoch, was bound to classical philosophy. The idea of the transmutation among substances was an assumption not only shared by the main philosophies of matter in Antiquity, but for Aristotle it constituted one of the most important keys for explaining chemical combination in terms of only the four elements and their qualities. If all bodies of the sublunar world were composed of air, water, earth, and fire, then one could transform one into another by changing the proportions of their constituents.

This basic philosophy permits us to understand how the identities of substances listed in the lapidaries, and in other works of this type, were so often confused with counterfeits or with such artificial products as glass. If one accepted the possibility of transmutations, then a sharp distinction between natural and manufactured products was clearly inconceivable. Hence, glass was often confused, or perhaps more correctly, set in relation to various crystals, metals, stones, and gems, which, in their turn, could assume characteristics similar to those it displayed.

In connection with the importance that the philosophers attributed to transmutation for explaining chemical reactions, another principle must be recognized for its enormous influence on the development of classical alchemy. We have already emphasized that one of the chief preoccupations of Greek philosophers was not to oppose art (i.e. man's operations) and nature. Attempts at re-evaluating the former were, in fact, directly conditioned by the ability to demonstrate its intimacy with the latter. *Art imitates nature* was thus a common saying or, as reported by Pliny the Elder's legendary history on the origins of metals and glass, nature itself generates art. In this regard, it is significant that in Plato's *Timaeus* the creator of the universe is called *demiourgos*, the artisan.

In the field of chemistry, the coexistence of art and nature was stressed repeatedly. Speaking of a sand with special properties, Theophrastus (c. 371–287), Aristotle's main disciple, for instance, noticed a means of imitating nature efficaciously in experiment and in technology [17], thereby outlining a theoretical principle that was to be carried out by classical alchemy.

Once they identified the relevant philosophical principles, alchemists could rely on an ample supply of

technical information. Even though sufficient direct evidence is lacking, the frequent references to the learning of the Egyptians, together with the Egyptian and mid-Eastern origin of most of the Greek alchemists, likely confirm the important influence of Egyptian arts and metallurgical techniques.

4.2 Bolus of Mendes

The earliest alchemist is Bolus of Mendes, also known as Pseudo-Democritus and long confused by late antique authors with the philosopher–atomist Democritus of Abdera (c. 470–380). Even though information is scarce concerning Bolus and his life, a rather corrupt lexicon compiled toward the end of the tenth century, identified him as a follower of Pythagorean philosophy and as the author of various works among which was one dedicated to “the sympathies and antipathies of stones.” The chronology of Bolus’ life is still more difficult to establish with any precision. He was long thought to have lived in the second century BCE. However, his use of oriental sources such as Zoroaster and Ostanès translated into Greek around the first century of our era situates his life in a later period.

In his *Letters to Lucilius*, the Roman stoic philosopher Seneca (4 BCE–65) still confused Bolus with Democritus of Abdera when he wrote [18]: “It seems to have quite slipped your memory that this same Democritus discovered how ivory could be softened, how, by boiling, a pebble could be transformed into an emerald – the same process used even to–day for colouring stones which are found to be amenable to the treatment!” The passage is revealing not only because it places the life of Bolus before 60 CE when the *Letters to Lucilius* were written, but shows how counterfeiting precious stones, primarily emerald, by using glass or rock crystal was not part of the craftsman tradition but was invented by an alchemist, or – as Seneca still confuses it, by a philosopher. Furthermore, as shown by the alchemical papyri of Leyden and Stockholm [19], the recipes for counterfeiting emerald represent a considerable part of late antique alchemical literature so that these recipes should have originated in Bolus’ work.

Even though available sources are indirect and fragmentary, it is not difficult to understand that Bolus was a figure of certain importance and originality in the panorama of this period. The dating of Bolus between the first century BCE and the first decades of the next century is important because we know, as Pliny the Elder recounts in detail [9b], that it was just in this period that glassmaking made important technological progress. Of course, it cannot be claimed that alchemy directly originated from the development of glassmaking but rather, contrary to what has been hitherto supposed, that close relations

were usually posited between the two arts as exemplified by the Christian philosopher Aeneas of Gaza (fl. fifth century CE) who wrote in *Theophrastus*, his dialogue on the soul: “Change of matter to a better state is not implausible for, among us, experts in materials, taking silver and tin, making their form disappear, melting them down together and colouring them, and so changing the matter in something grander, have produced excellent gold. Again, sand is scattered and soda is abundant everywhere, but human skill has made glass out of them, new and transparent” [20].

4.3 Glass and Counterfeited Stones

As already stressed, the art of glassmaking offered a splendid example of how common materials could be transformed by the furnace into a noble and brilliant material (Figure 3). This quality became apparent in the counterfeiting of precious stones. During the Hellenistic era, gems rapidly became luxury items, which were particularly sought after for their virtues. Pompeius Magnus (106–48) and Julius Caesar (100–44) were the first to build up important collections. During his third triumph (61 BCE), Pompeius brought to Rome what he believed to be his most precious war booty, the *myrrina vasa*, extraordinarily beautiful vases made of such a precious material that two generations later the Emperor Nero (r. 54–68) managed to ensure for himself one single bowl at the astronomical price of 1 000 000 sesterces. Without the help of archeological evidence, the identification of *myrra* has been so problematic that for a long period this mysterious substance was thought to be *millefiori* glass [21]. Only recently has it been demonstrated beyond doubt that *myrra* should rather be identified with fluorite.

Given the exceptional rarity of this mineral, Pliny thus reported that glass was used to imitate and counterfeit *myrra*. In view of the new spreading passion for gems and the peak of perfection reached by Roman glassmakers, Pliny mentioned in several chapters of his *Natural History* [9c] “how to make genuine stones of one variety into false stones of another” while lamenting that “to distinguish genuine and false gemstones is extremely difficult.” In addition, he mentioned the existence of treatises (*commentarii*), whose authors he preferred to omit, which gave “instructions how to stain crystal in such a way as to imitate smaragdus and other transparent stones, how to make sardonius of sarda, and other gems in a similar manner.”

Likewise, Pliny mentioned treatises devoted to glass. The circulation of this literature is of the greatest importance because it attests to the existence of authors who decided to write on topics that, for centuries, had been either kept secret or treated in general and encyclopedic works such as Pliny’s. The diffusion of this literature was



Figure 3 Pharmaceutical and chemical (?) glassware found in the Casa del Fabbro in Pompeii during the first half of the twentieth century. All items destroyed during WWII. Source: Courtesy Soprintendenza Archeologica di Pompei.

certainly justified by the amazing dexterity reached by Roman glassmakers in imitating precious stones.

More common stones were also worked in such ways that they soon became luxury objects. Rock crystal was so highly regarded by the Romans that at the time of Pliny a single dipper was paid 150 000 sesterces by “a respectable married woman” [9d]. As a consequence of these follies, the manufacture of imitation and counterfeit was encouraged. “Glassware, said Pliny [9e] on this matters, has now come to resemble rock-crystal in a remarkable manner, but the effect has been to flout the laws of nature and actually to increase the value of the former without diminishing that of the latter.” That fake crystal artifacts did not cause prices to fall was probably due to the perfection of the counterfeits, which, without the help of chemical analysis, often remain today difficult to distinguish from true ones. By combining glass to crystal Roman artisan were able to imitate beryl, a gem particularly admired also because of his virtues [9f].

By the end of the second century CE, the connection between glassmaking, gold, and precious stones was

embodied in the description in the Apocalypse of Saint John [18, 21] of the new Jerusalem where we read: “And the building of the wall thereof was of jasper stone: but the city itself pure gold, like to clear glass.”

As for opal, Pliny said that “there is no stone which is harder to distinguish from the original when it is counterfeited in glass by a cunning craftsman. The only test is by sunlight” [9g]. Also *carbunculi* (rubies?) were “counterfeited very realistically in glass, but, as with other gems, the false ones can be detected on a grindstone, for their substance is softer and brittle” [9h]. Whereas “no gemstone is more easily counterfeited by means of imitations in “glass” than “topaz,” Pliny added [9i], many other gems such as jasper, zephyr (?) were mentioned by him in connection to glassmaking. The imitation industry must have been flourishing at the same time when glassblowing was a widespread technique because, some decades before Pliny, the Roman encyclopedist Varro (116–27), noted in his *Saturae Menippeae* [22] that “to an inexperienced eye, a shell sometimes looks like a pearl, and glass like emerald” [22]. These fraudulent practices became

eventually so common that the first Church fathers often took it as an example in their writings to show the deceptive nature of glass products.

4.4 An Elusive Art

If imitation was as ancient a practice as glassmaking itself, treatises explicitly devoted to this art must have been relatively recent as no reference to them can be found in earlier sources. This literature, which would eventually be embodied in alchemical recipes, was thus contemporary to the extraordinary development of glassmaking. Although it is impossible to ascertain a direct relation between them, the number of distinguished authors who wrote extensively on the marvelous nature and history of this material makes us conclude that the progress achieved in the art also inspired a systematic reflection on the influence of glassmaking upon the traditional philosophy of matter.

After enumerating gems and their imitations, Pliny concluded his *Natural History* by addressing his reader with the following interesting statement [9j]: “We must not forget to mention that gold, for which all mankind has so mad a passion, comes scarcely tenth in the list of valuables, while silver, with which we purchase gold, is almost as low as twentieth.” Because alchemy, from the Middle Age onward, has been principally identified with the art of transmuting vile metals into gold or with the *chrysopoeia*, the hierarchy of valuables mentioned by Pliny placing gems in the first nine positions, provided an authoritative reason why craftsmen preferred to produce false gems and precious stones rather than embarking in what would eventually be the main occupation of alchemists. In addition to this argument, the importance of which is usually underestimated, the existence of a literature on glassmaking reveals that it was in this context that the first systematic ideas upon the possibility of imitating minerals took place for the first time.

The fact that Pliny deliberately chose not to mention the name of the authors of these treatises shows that a debate on the relation between natural and artificial stones was particularly lively and that the ambition of creating gems by the chemical arts was regarded with contempt by traditional naturalists. Inspired by a conservative philosophical standpoint Pliny, like Seneca, despised the pretentious attitude of these craftsmen who contended with nature for the act of creation. The position held by ancient philosophers seemed to be incompatible with the proliferation of opinions and practices, which, in the eyes of Pliny and Seneca, revealed the cultural and moral decadence of their contemporaries. The high social status of both authors justified their

negative attitude toward the *Commentarii* and their authors, but one wonders whether their perceptive attention on the recent technical progress was not a sign of the power of attraction they exerted on the intellectuals of the time.

Additionally, there were authors who held a different opinion to develop new theories on the properties of matter by taking the chemical arts as point of departure. This was the case of the enthusiastic followers of the Pythagorean philosophy, which spread in Rome as early as the first century BCE and made systematic efforts to combine the arts with magic and philosophy. While describing the problematic properties of the diamond, Pliny remarked [9k]: “Now throughout the whole of this work I have tried to illustrate the agreement and disagreement that exist in Nature, the Greek term of which are respectively ‘sympathia’, or ‘natural affinity’, and ‘antipathia’ or ‘natural aversion’. Here more clearly than anywhere can these principles be discerned.”

Pliny probably referred to a work entitled *Peri antipatheion kai sympatheion lithon* which evoked a doctrine that was exerting a considerable influence on natural philosophy. The author of this work is uncertain, although, given its astrological contents, Bolus of Mendes seems the most likely candidate [23]. Whatever the real identity of the alchemist was, it is important to point out the connection between the appearance of Bolus’ works and the development of glassmaking, an art which enjoyed both a high social reputation and a considerable “philosophical” importance. Such a reputation, reflected in the publication of treatises devoted to this topic, reached its peak during the first century CE when Pliny associated this literature with fraud because he felt the threatening effects of its pervasive diffusion. The chronological coincidence between the appearance of the work of the Egyptian alchemist and the progress made in glassmaking is of crucial importance because Bolus was the first author who believed that one metal might be made from another [23] and clearly referred to the possibility of the alchemical operation of transmuting substances by giving practical instructions.

5 The Byzantine Connection

Whereas many Latin authors explicitly referred to alchemical authors during the first two centuries CE, the Latin West witnessed a rapid decline of scholarly knowledge after the Barbarian invasions and fall of the Western Roman Empire. From the third century CE onward, the pursuits in alchemical research thus remained confined within the Greek and then Byzantine tradition.



Figure 4 *Garden of Eden* mosaic decorating the vault of the Galla Placidia Mausoleum, Ravenna. First half of the Vth century (after 425).

Glassmaking progressively migrated from the Roman centers of production to the south Eastern capital and cities. Together with several Syrian centers, the Alexandrine area and Ravenna (Figure 4), Constantinople represented from the first half of the fourth century CE to the end of the sixth a cultural site capable of assuring, though briefly, favorable conditions for scholarly and technical research.

In this favorable context, the presence of an important community of glassmakers is attested in Constantinople. Unfortunately, apart from massive archeological remains, our knowledge of the Byzantine glass production and of its uses is confined to exceedingly few literary sources, most of which are late and medieval. But spectacular evidence for a flourishing glass industry during the early centuries (fourth to sixth centuries CE) of Byzantium is undoubtedly the monumental mosaics which adorned the newly conceived basilicas and mausoleums.

The case of alchemy shows that Byzantine culture played a crucial role in directing the heritage of the

Greco-Egyptian tradition onto a new path. The corpus of ancient alchemical writings was collected probably for the first time in Constantinople between the seventh and the beginning of the eleventh century, when the *Codex Marcianus Gr. 299* was compiled. This manuscript, preserved in the Biblioteca Marciana in Venice, is the primary source of most of the known ancient alchemical texts. It includes not only the writings of Pseudo-Democritus and Zosimus of Panopolis (third to fourth centuries), among others, but also of Byzantine authors such as Stephanos of Alexandria (c. 550–before 638) and lists the titles of lost texts attributed to authors bearing the names of the Byzantine Emperors Justinian (r. 527–565) and Heraclius (r. 610–641), indicating that alchemy attained an unprecedented high cultural and social status in Byzantium.

The remarkable strength and prestige of the Byzantine alchemical tradition is further evidenced by the *Epistle on the Making of Gold* of Michael Psellos (1018–after 1081), the most influential intellectual of the period, where metal transmutation was accounted for in terms of the theory of the four elements [24]. Although this work does not contain anything particularly original, it demonstrates that alchemy was an integral part of high Byzantine cultural circles where, along with astrology, alchemy was likely included in higher education.

The Byzantine contribution to the alchemical corpus consisted of several recipes dealing with, among other things, glass-making, the coloring of precious stones and the manufacture of pearls. It is probable that the prosperous glass industry and its prominent role in the architectural decoration of Byzantine churches and basilicas were sources of inspiration for the alchemists in their search for the transmutation of matter. This hypothesis finds a confirmation in a work of Stephanos of Alexandria included in a manuscript, the *Parisinus Ms. 2327* of the Bibliothèque Nationale de France, where the author described in several recipes the fabrication of precious stones by colored glass and enamels.

Many of these recipes were probably coming from the Greek-Egyptian tradition. Without textual evidence, however, it is impossible to determine what exactly was added in Byzantium. It is interesting to point out once again that the progress of glassmaking went hand in hand with the development of alchemy (Figure 5). The earliest explicit definitions of this discipline as *Sacred art* during the fifth century coincided with a widespread experimentation with new glass techniques. It is therefore not surprising that the definition of transmutation set forth by Aeneas of Gaza took glassmaking as his point of departure.

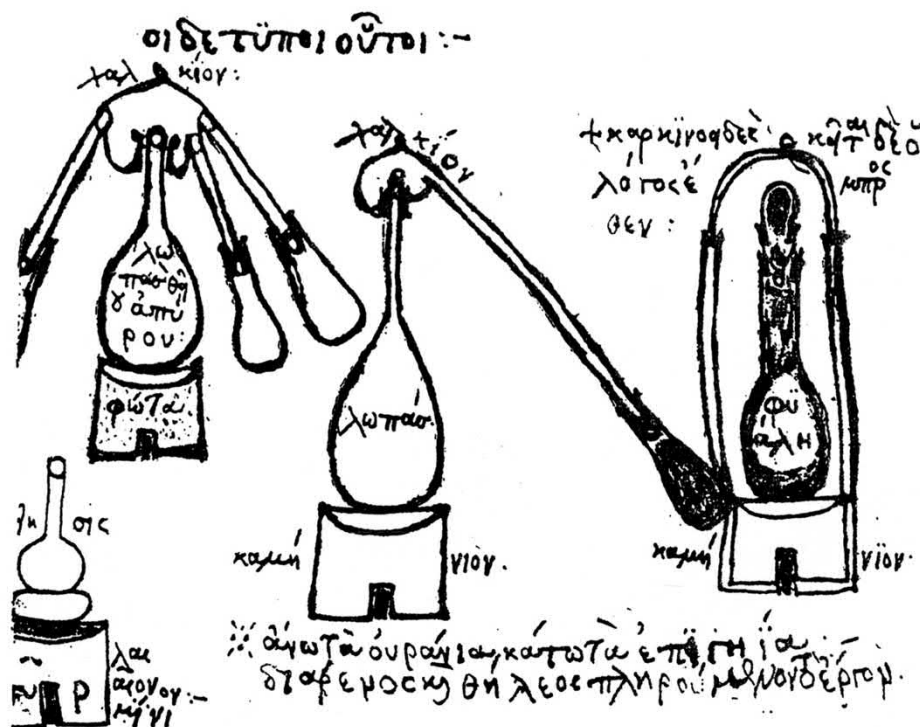


Figure 5 Glass alchemical alembics illustrating the Codex Parisinus 2327 thirteenth century manuscript of Mary the Jewess' *On Furnaces and Instruments* (c. second to third century) as quoted by Zosimus of Panopolis [25].

6 Perspectives

The Egyptian glassmaking tradition survived in Hellenistic Alexandria, exporting both technical know-how and theoretical insights to Palestine and, during the Roman Empire, along the Mediterranean coastline. Such an influence explains the Greek alchemists' admiration for Egyptian culture. The survival of the *Marcianus graecus* ensured a future to the Greek alchemical tradition and its acquisition by the Byzantine cardinal Bessarion (1430–1472) probably favored its study in the West after 1468 when it was donated to the Biblioteca Marciana in Venice. However, interest in alchemy and in its connection with glass had then already been raised in the Western and Latin culture. Ideas circulated in the Mediterranean along with commodities and technical knowledge. Thus, the development of alchemy, like glassmaking, was the result of a fusion of multicultural traditions. Inasmuch as ancient alchemy was characterized by a remarkable attention to the chemical arts, we must always bear in mind that its first definition regarded it as a “holy” and “sacred” art, and that its philosophical and spiritual background were no less essential features of its identity than divination and magic were connotative elements of astrology. This characteristic of ancient alchemy once more underlines a debt to

Egyptian culture and religion. Religion, philosophy, and chemical know-how converged into the creation of a new body of knowledge, which remained prosperous even when all the other natural sciences were declining during the Hellenistic epoch and Late Antiquity. Historians of ancient science have neglected the remarkable development of chemical arts and the fecund connections they entertained with their culture. The history of ancient glass shows by contrast how useful it is to follow the impact of this technology among learned circles and how its breakthroughs have inspired philosophers of nature and alchemists alike to develop new ideas on the architecture of matter.

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10.5

Ancient Glassworking

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1 Introduction

Glassworking was a significant component of ancient technology. Tracing its evolution thus contributes to a better understanding of ancient societies especially since glass became a ubiquitous material of dual practical and aesthetic interest. The history of ancient glassworking is in addition relevant to modern technology or even to marketing. Whereas industrial processes such as flame finish (Chapters 3.12 and 6.7) and brand packaging still rely on innovations dating back to antiquity, most of the methods practiced today in art glass studios were already in use in the first century of our era.

Glass was a by-product of metallurgy and, particularly, of ceramics. Therefore, it should come as no surprise that glass artifacts initially imitated metal and pottery work. It took of course some time to recognize the original properties of the new material and to take advantage of them in new processes. Some techniques are still well known so that historians are paying more attention to those that disappeared, often after having given rise to outstanding masterpieces. Ancient glass has kept various defects as a memory of its fabrication. Toolmarks are important because traces of cutting, pinching, stretching, twisting, indenting, grinding, or polishing relate to the processes themselves. In addition, air bubbles, folds, or chillmarks represent a frozen image of the movement of the glass during shaping. But the interpretation of these features is not always unambiguous because blowing, sagging, and pressing can, for instance, cause bubbles to stretch in the same direction. As for idiosyncrasies like lopsided ribs and scratches in unexplainable places, they too carry information that has to be unraveled.

Current research on ancient glass-forming techniques thus also relies on theoretical reconstructions, production of replicas, and ethnographic research. All three require experiments, be they as confirmation of the feasibility of the suggested technique or as test of ideas for making reliable replicas. Any theoretical reconstruction of a technique needs to explain all the details and idiosyncrasies provided by the ancient artifact and to agree with the technological shelf available at the time and location of its production. If experiments are needed to test the feasibility of a hypothesis, they do not need to generate a perfect replica. Successful experiments are instructive only insofar as they demonstrate the feasibility of a production method. They do not represent incontrovertible evidence for the proposed technique. Not only more than one method might achieve a specific result but, like their modern counterparts, ancient artisans were likely wont to develop their own way of doing things.

It is beyond the scope of the present chapter to review all these aspects and, in particular, all diverging propositions that have been discussed in the literature. Rather, our goal here is to stress the inventiveness and artistry of ancient glassworkers by showing how they took advantage of the unique properties of glass that are discussed in many other chapters of this Encyclopedia. Material constraints will first be presented especially in terms of viscosity, temperature, and expansibility. That for 15 centuries rather viscous glass was shaped will be illustrated by techniques such as core forming, casting, and mold pressing. Excluding flat glass, which is dealt with in Chapter 10.8, the new possibilities offered by blowing will then be described. Workshops and the social and economic aspects of glassworking will finally be discussed along with some of the reasons why glass met with so much success in antiquity.

In preamble, however, it needs to be stressed that a major problem of reconstructing early techniques is that

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a glassworking furnace predating blowing has not yet been identified beyond doubt. Although potter kilns could have been used for firing glass in molds and preparing flat glass [1], accessible, open heat sources were needed for hot manipulation and tooling. Use might have been made of mobile firepots like those used by Egyptian metal smiths in the third millennium BCE or of shaft furnaces that deteriorated without leaving a trace. One would then understand why a workshop at Rhodes of the Hellenistic period (third to first centuries BCE) showed no trace of a furnace although tools and waste from bead and vessel production as well as thousands of beads, canes, and chunks of raw glass were found [2].

2 Basic Features of Glass Shaping

2.1 Physical Conditions

Every glass-making operation is performed under well-defined conditions characterized by fixed viscosities (Chapters 1.1 and 4.1) and, therefore, fixed temperatures for a given composition (Figure 1). But neither concept existed before the seventeenth century. Whether glass was made from raw materials or simply shaped, it was its hotness and workability that were gauged from its color and its movement on a tool. Of particular importance were three colors interpreted as *heat* indicators by Late Bronze-Age glassmakers: *glowing red*, *glowing*

green/yellow (meaning perhaps orange/yellow), and *glowing golden yellow*, the highest heat they could reach [3].

We now know that a typical Roman glass (Chapter 10.3) was sufficiently homogeneous at 1050–1150 °C, the range at which it was gathered from a pot or a tank furnace. The outer skin of the gob needed to be cooled to become a bit more viscous for blowing between 970 and 1020 °C, the rather narrow range where the glass was neither too rigid nor too soft so that shaping it on the blowpipe was readily controlled. It became possible to draw long, thin canes at around 930–950 °C when a thread could be trailed from one tool onto or around another. Above about 900 °C, one could have pinched, poked, bent, pulled, and manipulated the soft glass with handheld tools or *marvered* it on a flat surface (i.e. roll it back and forth). Flattening was an extreme form of sagging. A sizeable chunk of raw glass began to deform and sag outwardly at about 830–875 °C. It lost its shape and flattened to an equilibrium thickness of about 0.7 cm (Chapter 1.4) while its edges contracted [1] and tended to become circular as a result of surface energy minimization. One piece fused to another from 715 °C whereas the lower end of the working range was about 600 °C, the temperature at which glass began to bend or sag under its own weight.

Glass adhered to metals and ceramics as long as both materials were hot. But a temperature difference was crucial to the success of operations: upon gathering, the tip of the blowpipe had to be cooler than the glass to let it contract around it whereas the opposite held true to let

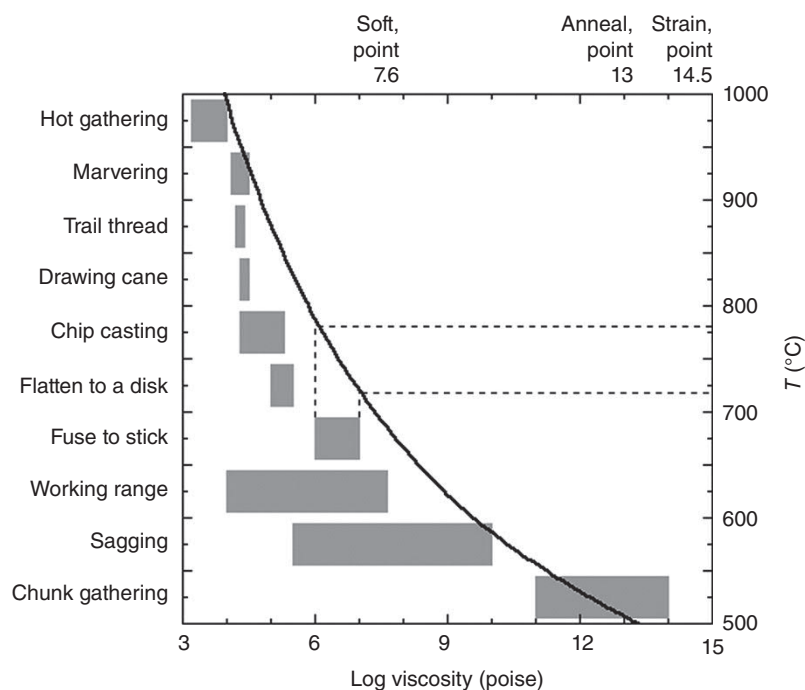


Figure 1 Viscosity ranges for glassworking operations and viscosity–temperature relationship of the typical Roman glass of the Embiez shipwreck (solid curve, P. Richet, personal communication). Temperature interval of fuse-to-stick operations indicated as an example.

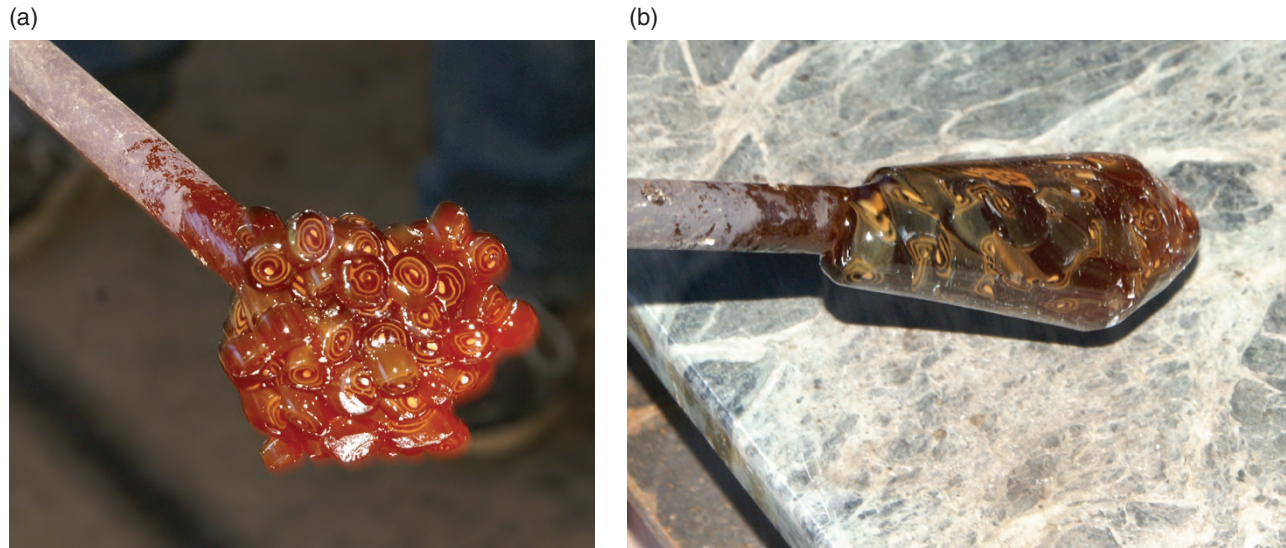


Figure 2 Gathering of 1–3 g mosaic glass *florets* (slices) on a blowpipe: final gather (a) reheated and marvered (b) after eight steps of pickup and reheating in six minutes. Source: Photos Arz.

chunks of “cold” glass stick to the pipe when they were picked up [4]. For gathering, the chunks had to be preheated to about 500 °C to avoid thermal shock. After each gathering, the glass on the blowpipe was shortly reheated to ensure the sticking of the next chunks picked up (Figure 2). At the end of the process, the jumbled mass was heated to higher temperatures to be marvered and shaped into a smooth piece, which could then be blown.

2.2 The Issue of Thermal Expansion

The fundamental glassworking step was annealing, which had to be performed at about 500 °C to prevent the accumulation of internal stress caused by the fictive temperature gradients created through the glass transition (Chapter 3.7). We do not know how and when it was realized that glass had to be cooled down very slowly after shaping, the larger the piece the slower the rates, or when dedicated furnaces or kilns began to be used for annealing. At least three different types of glassblower furnaces are known from the Roman period, one circular and two rectangular, but the function of the latter has not yet been identified clearly. Ancient glassblowers could have used the heat of piles or baskets of hot ashes, olive pits, or the like for annealing, but the cracks observed in many ancient glasses point to often insufficient relaxation of internal stresses. Cracks could also be caused by thermal expansion mismatch in pieces made from two or more glasses of different chemical compositions (Chapter 3.5). In the Late Bronze Age, colorants were usually added by the producers of the raw glass [5]. The composition

changes induced in this way were thus minor so that expansibility conflicts were not likely to create a problem for the brightly colored polychrome objects and vessels fashionable in Western Asia and Egypt, especially in view of the low shaping temperatures [6]. In Mycenaean Greece, where glassworking was also common in this period, the artisans rarely combined different colors within one piece. They used almost exclusively blue glass [1], which was also the preferred color at many Late Bronze-Age working sites in Central Europe and north Italy. Pliny (23/24–79 CE) reports that in his days glass was frequently colored in secondary workshops [7], which would have had the advantage that the glassblowers themselves could control the process and the danger of strain be kept to a minimum [6].

2.3 Molding Processes

Molding was invented long before blowing. In the Late Bronze Age, the most widely used mold materials were stone and especially pottery, which shrank, but less than glass, and then also plaster. The higher the temperature and the longer the cooling, the greater was the danger that the glass would stick to the mold. Although pottery molds without undercuts were reusable, a *separator* substance was needed if the glass was not removed before annealing. Corundum (Al_2O_3) was one substance used for this purpose as indicated by the traces of this highly refractory oxide found in Greek terracotta molds dating from the late fifth or early fourth century BCE [1]. Bone ash, a substance readily available, might have been



Figure 3 Rotary scratches on the interior of a ribbed bowl fragment (Frankfurt/Main, Arch. Mus., inv. α24292) (preserved height 7.2 cm). Source: After [10].

another strong separator [1], as could also have been soot although no trace of it has been found in the rare ancient molds extant [8].

If glass sagged over a convex mold, it had to be lifted off before annealing to avoid cracking through shrinking upon cooling. Plaster molds had several advantages although they could be used only once. Plaster did not undergo volume changes with temperature and its dissolution in water made removal of the mold easy after annealing. In addition, fresh plaster contained some moisture – the so-called crystal water – that evaporated upon contact with the hot glass and acted as a separator ensuring a shiny glass surface [6]. Because of the weakening effect of this water loss, the mold tended to fall apart during or after annealing. A solution to this problem was thus to place the mold in a sturdier container, which provided extra strength during use. Likewise, moist wooden paddles for shaping and plungers for pressing glass created a shiny surface through the evaporation of moisture upon contact with hot glass.

Glass is not a good heat conductor (Chapter 4.5). Whereas cold glass can fracture by thermal shock when touching a glowing-hot blowpipe or pontil, *chill marks*

result from the sudden contact of hot glass with a cold marver or mold. Chill marks appear as wrinkles or ripples on the surface of the glass [9] or as the concentric depressions sometimes seen on the walls of Roman square bottles shaped freehand on a marver. Rotary scratches with a definite beginning and end are often found on shiny surfaces of the inside and bottom of non-blown ancient glass vessels such as Hellenistic sagged vessels and ribbed bowls (Figure 3). The scratches were interpreted as grinding or polishing marks until microphotos revealed that they could be accompanied by shortened *horseshoe chatter marks*, a phenomenon observed after a mishap with hot glass (Figure 4). Because they are found on vessels subjected to a rotary motion either during their shaping or when lifted off the molds, the rotary scratches are now ascribed to friction while the glass was hot, either by protruding particles of ancient tools or molds or to inhomogeneities in the glass [6].

3 Early Shaping Methods

3.1 The Ceramic Connection

Before the invention of blowing in the first century, glassworkers made a limited use of hot glass for both shaping and decoration. Crushed glass and small chunks of raw glass heated at the tip of a handheld tool sufficed for the production of most artifacts. Artisans actually took care not to overheat a piece, which would have been lost if the glass melted. In the Late Bronze Age, the ability to build melting furnaces was likely less problematic than long thought. Whether the Egyptian furnace at Amarna was a primary glassmaking furnace or not, a replica could reach 1150 °C [11]. Hence, difficulties for remelting ingots were not the reason for low-temperature shaping there and in nearby Qantir where primary and secondary workshops were located in proximity [5].

At Amarna and Qantir, glassworking and faience production took place in parallel. The first craftsmen working with true glass had worked previously with faience and other vitreous materials. Consequently, they built on techniques familiar to them. Sintering, for instance, was a ceramic technique to transform a powder into a coherent mass without melting. The raw material was layered into or over a mold, dried, and fired in a kiln. Similarly, fine crushed glass could be layered into or over a mold or core and sintered. Another early technique that had its roots in ceramics was the *pressing* of crushed glass and heat-softened chunks into molds [6]. Extant artifacts show that the glassworkers gradually improved manufacturing techniques, discovered new properties of the material, and invented novel tools and techniques to make use of those properties.

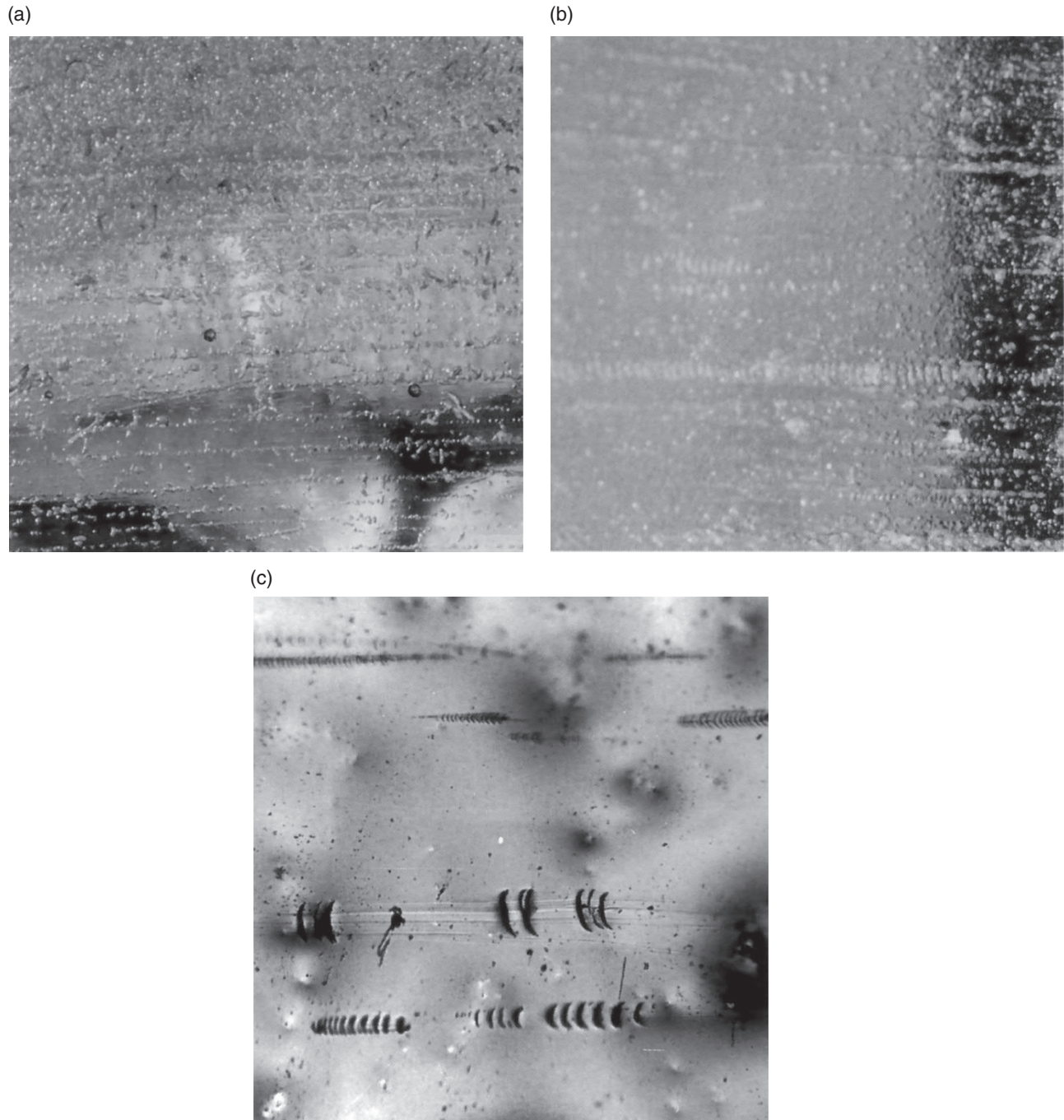


Figure 4 Rotary scratches exhibiting *horseshoe chattermarks* so much shortened that they almost look like vertical lines: a close-up of the fragment in Figure 3 (a) and two micrographs, one of the fragment in Figure 3 (b) and the other of a mishap in hot glass (c) at Schott Glas, Mainz (Germany).

3.2 Core-Forming

The earliest glass vessels were made by core-forming, a generic term for a number of techniques that involved deposition of glass on a rigid core that was subsequently scraped out. In the Late Bronze Age, the deposition of cold pieces of glass was a Western Asiatic specialty.

Vessels known from several sites display colorful figural scenes and zigzag patterns created with short segments of opaque red, yellow, blue, and white canes with circular sections. The individual pegs or canes look as if they had been held together by bitumen, which would have burned off during firing [3]. The vessel's exterior, which was

exposed to the heat, fused better than the interior stuck to the bitumen coating of the core. All these vessels lacked handles and applied decoration, which would have required tooling while the glass was hot [12].

Most Western Asiatic and Egyptian core-formed and rod-formed vessels carry tooled decoration applied to a monochrome underground, the “body” of the vessel [1, 13]. It has been often claimed that the core was immersed into a pot filled with hot molten glass to produce the body. Archeological research and experiments [14, 15] do not support this statement, however, because pots able to withstand hot molten glass are not known at Late Bronze-Age sites [5]. Those used at Amarna and Qantir were much too small to accommodate core-formed vessels that could be from 16 to 26–40 cm in height, like the amphoras found in the tomb of the pharaoh Amenhotep II (r. fifteenth century). Pots for remelting glass actually did not become common until the third century CE, but they still would have been too small. Moreover, the strain induced by a mass of hot molten glass cooling and shrinking around a core would have induced cracks, a phenomenon that has not been attested.

An ancient core-formed bottle from Iraq provided important clues as to manufacturing techniques in the Late Bronze Age [12]. Experiments show that a mold-formed core made from a 10:1 mix of sand and clay, that is pre-fired at about 815 °C, works well [14, 15]. It was mounted on a metal *mandril* (supporting rod), coated with a liquid slip of the same materials, and fired at c. 700 °C after which the core was thoroughly wetted with water to let finely crushed glass stick to it like wet sand. Upon sintering at about 590 °C, the glass glazed over and fused to the core. After further heating up to about 860 °C, successive layers of crushed glass were added by rolling the core back and forth on a flat surface in a way that shaped the vessel and smoothed its wall. This process accounts for the observation that the glass of the bottle from Iraq was layered parallel to the surface of its wall and that bubbles trapped in between these layers were spherical because the glass was not stretched in a particular direction while hot [12]. The handles and decorative trails were made with colored canes prepared independently, while zigzag patterns, festoons, feather patterns, and the like were created with a pointed tool or hook that dragged the threads up and/or down.

Crucial to the success of these experiments was the use of a furnace with a vertical heat chamber, which was open at the top (Figure 5). Because of vertical heat rise, the artisan could manipulate the glass-coated core and the glass canes while controlling the temperature on the relevant side of the piece by a slow rotation of the mandril. In addition, a slit in one side of the opening at the top of the furnace made it easier to work lower down in the heat, for example, when the decorative glass threads were dragged back and forth.

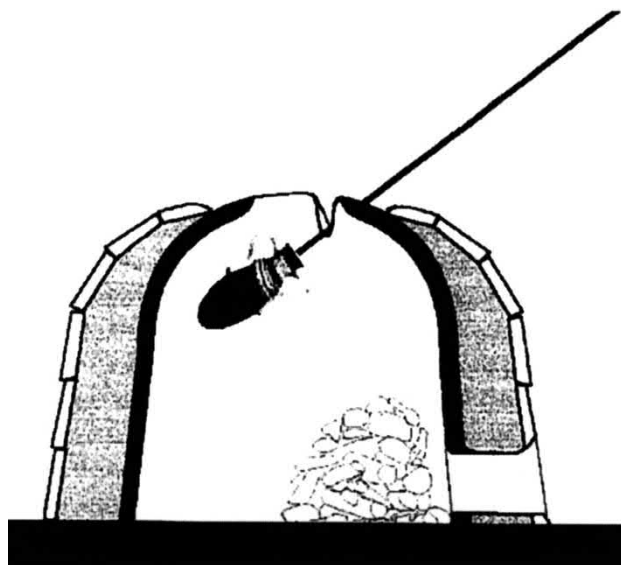


Figure 5 Core-forming furnace open at the top (height 52 cm) as designed and drawn by D. Giberson. Source: After [10].

Although vessels had become much smaller, core-forming enjoyed a prolonged revival from the mid sixth through the end of the first century BCE. [1, 13]. Now, the body was sometimes made from a hot trail of glass wound around the core, with the decorative trails going in the opposite direction [1]. This technique was probably made possible by the discovery that small pieces of pre-heated raw glass could be picked up on the glowing tip of a solid metal rod and sufficiently heated to create a gob of glass from which trails could be wound around the core. The furnace would still have been open at the top. Working directly above, and at times in the heat, the artisan could manipulate core and trail simultaneously, while controlling the temperature of both. The orientation of the heat with respect to the core made it possible to apply an endless thread of glass as observed in the Hellenistic period.

3.3 Casting

In the Late Bronze Age, glassworkers developed the *chip casting* technique reminiscent of faience firing in that its first step was the filling of a mold at room temperature with a finely crushed glass [1]. Upon firing at about 870 °C, more crushed glass was added with a funnel-shaped sprue to fill the mold entirely, as shown by funnel remains on the rim fragments of glass-coloring pots at Qantir [16]. The best evidence for chip casting is provided by the headrests of Tutanchamen (r. fourteenth century). Weighing about 2 kg, the largest one was cast in one piece 17.5 cm high, 28.3 cm wide, and 10 cm deep [17]. The molds would have been made from the same materials as the glass melting

pots used at Qantir, which were lined with a parting layer and specially designed to optimize heat conduction from the outside. A similar parting layer in the molds would have ensured that only a final surface polishing was needed to remove any roughness after annealing [5, 17].

In antiquity, chipcasting was primarily a means of making a single hollow object after a wax model had first been made. Early cast vessels made of transparent colorless glass evoking rock crystal were precious, individual pieces, often imitating the shapes of silver vessels decorated with petals that were convex on the exterior and concave on the interior. Both the wax model and the mold were destroyed in the process: the wax model when the artisan burned it out of the mold in preparation for casting and the mold after the piece was fired. Made of plaster, the mold was broken away to extract the piece.

3.4 Mold Pressing

An important evolution took place when the artisan used a moist wooden plunger to press a gob of glass inserted as hot as possible into a mold to shape at the same time the external and internal surfaces of a vessel, whether plain or decorated with relief. Solid objects, such as amulets, inlays, beads, pendants, and other small artifacts could be pressed in reusable open molds, either with sintered crushed glass or with small pieces of softened glass [1, 13]. Again the technique was closely related to faience. In Bronze Age Egypt, ceramic molds were used, but Mycenaean (Greek) beads and inlays were usually made in steatite molds that could have been used as well for the production of gold ornaments. The numerous techniques used in antiquity for the production of beads and other small objects have been extensively discussed [1, 18] so that they will not be included here.

More important was another form of mold pressing that supplanted the time-consuming casting in the fourth century BCE because the same kind of production could be achieved faster. This was not possible for vessels with a decoration that was convex on the exterior and concave on the interior. However, by far the majority of glass vessels decorated with relief on the exterior now had smooth interiors that presented no obstacle to pressing in concave molds.

One created easily exterior ridges by making a simple groove or drawing a thin line in the interior of the mold [19]. Glass vessels decorated with high relief are commonly assumed to have first been blown and their decoration cut after annealing [19]. But the walls of the ancient vessels are entirely smooth between the elements in high relief and show no signs of grinding or polishing. Hence, the high relief was probably mold-formed [6, 10]. A wax model with the decoration applied to the surface served to create a sturdy plaster mold, which was filled with hot glass. While the mold was turned with some device, a moist wooden

plunger pressed the glass into it. After annealing, the plaster mold fell apart. Simple motifs, ridges, and letters (in reverse) could be engraved directly into the mold.

3.5 Rotary Mold-Pressing

When the mold was put on a turntable or potter's wheel (Figure 6), the combination of vertical pressing and rotary rubbing made pressing at relatively low temperatures possible and ensured a more uniform distribution of the glass for open vessels with a simple cylindrical or outward curving profile. The earliest evidence for the technique comes from Ionia (southwest coastal Turkey) and Greek Macedonia [20] where colorless glass bowls decorated with fine vertical ribs or petals imitating silver work appeared in the middle of the fourth century BCE.

Mold-forming is familiar from the production of mold-made Hellenistic pottery, thought to have been invented in Athens in the last quarter of the third century BCE. The main difference was that potters used molds for mass production, whereas glassworkers could not reuse molds with decoration in relief because they disintegrated and/or had to be broken away from the finished product.

Rotary mold-pressing was also used to *case* glass, i.e. to fuse one layer of glass with another usually of a different color. Cased glass cups, often with a paper-thin, opaque white lining became a specialty in the second quarter of the first century CE. The lining enhanced the transparent colored glass on the exterior. Whereas the layers of colors

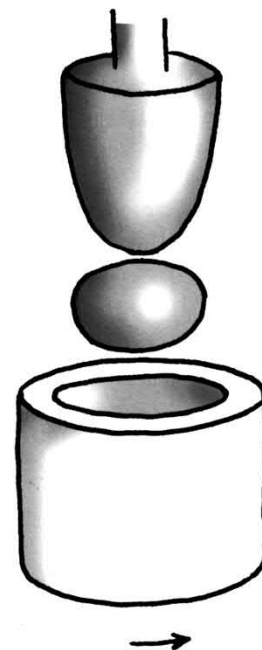


Figure 6 Rotary pressing: gob of hot glass pressed with a moist wooden plunger in a turning plaster mold. *Source:* After [10].

in an experimental bowl are thick, mold-pressing made it possible to create an internal lining even thinner than achieved by blowing. In that case, two plungers were needed, one for the external glass of the vessel and another, slightly smaller, for pressing the internal glass [10].

3.6 Rib Making

Toward the beginning of our era, the most popular type of glass vessels were *ribbed* bowls [1, 13, 19]. They are thus regarded as a hallmark for the Julio-Claudian period. No two bowls are exactly the same because irregularities in the length and placement of the ribs show that each one was tooled individually [19]. The ribs were shaped either while a mass of hot viscous glass was sagging over a convex mold placed on a slowly turning turntable (Figure 7) or they were pinched into a pre-formed disk of glass, which was then sagged [21]. Ancient ribbed bowls can be replicated with both techniques. The former yields relatively thick ribs that often curve slightly in one direction and have lopsided profiles like the mass-produced ancient bowls of natural bluish green or more expensive colored glass. The latter yields in contrast thin ribs, usually vertical, like those seen in ancient ribbed bowls executed in expensive luxury glass [21].

A monochrome ribbed bowl could be tooled on a turntable in one or two minutes. No polishing was required because the glass was smooth except for occasional rotary scratches [6, 10]. The rims often show toolmarks from pressing the glass against the mold to stem the flow.

Grinding the exterior of the rim area, which became common in workshops in Italy and northwestern Europe during the first century CE [19], would have required no more than 5 or 10 minutes. Certain mosaic glass ribbed bowls suggest that the distortion of the pattern was not a problem because it made the glass look like a semiprecious stone [1, 19].

3.7 Coiling and Striping: Reticella Vessels

Reticella (network) vessels were made from the eponym *reticella* canes and trails created by application of one or two thin monochrome canes to a transparent, colorless bit of heat-softened glass, which was then twisted and lengthened (Figure 8). For the *spiral* bowls, made from the second century BCE, hot and pliable trails were coiled around a convex mold placed on a turntable (Figure 8). For the *parallel* reticella vessels, [13, 19] produced a little bit later, cane segments were first fused parallel to each other to form a striped disk which was then sagged over a stationary convex mold. In the former, the spiral trail and the bowl were created simultaneously, the trail going from the bottom center toward the rim [1, 10]. The rotary scratches occasionally observed on both types of reticella bowls are an indication that the glass was still hot when it was scratched, either during the turning of the mold or when the vessel was lifted off (Figure 8).

A bowl made from three alternating trails would have required four artisans: three for holding and turning the hot bits of glass of the reticella trails and one for

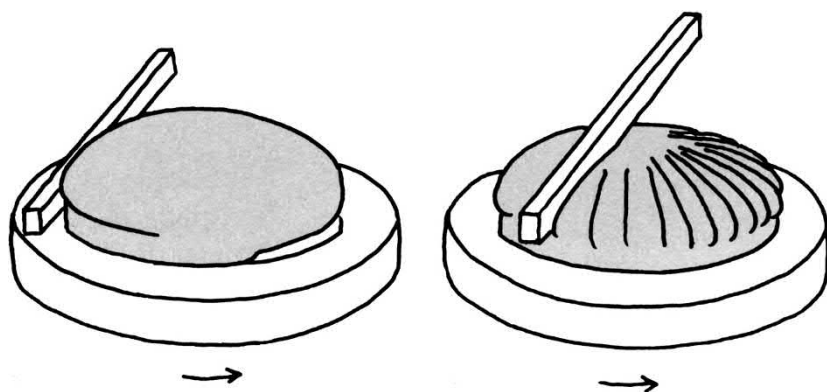


Figure 7 Making of a ribbed bowl: sagging or flowing down of hot glass over a slowly turning convex mold; rim pressed against the mold, cooling the glass and thus stopping its flow; interstices between the ribs then pressed, pushing up the glass on one side with mold turning. Source: After [10].

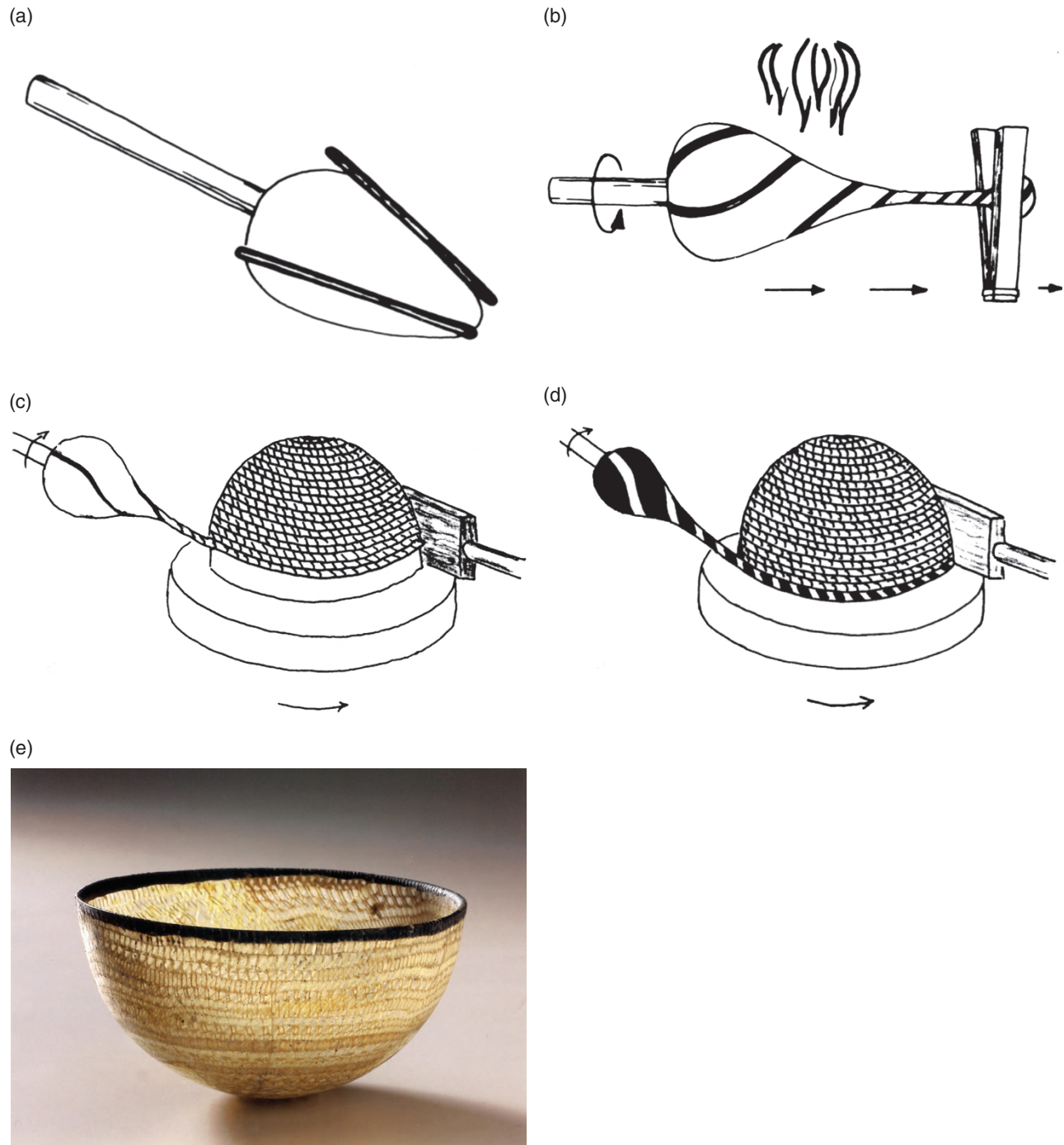


Figure 8 Making of spiral *reticella* vessel: drawing of the thread from a rotating conical bit of colorless glass on which two colored canes have been deposited; coiling of the thread around the mold, and final attachment of the rim made of a thicker thread of dark glass (Source: After [2]). Spiral reticella bowl (height 7.0 cm, rim diameter 12.8 cm.). Probably second half of second century BCE. Stuttgart, Landesmuseum Württemberg, inv. Arch 97/W73. Formerly Ernesto Wolf Collection. Source: After [1].

turning the wheel and pressing the trails against the mold with a moist wooden paddle to obtain smooth walls on either side [6]. No grinding or polishing was possible because the canes were not protected by transparent

colorless glass. A striking feature of spiral reticella bowls is the uninterrupted winding of several-meter length that could be involved, which would have been very difficult to achieve with a stiff thin cane.

3.8 Miscellaneous

Apparently invented in the early second century BCE, a curious technique was used exclusively for the production of small round, lidded boxes known as *Cretan pyxides*. As done by the potter's hands, a moist wooden paddle was applied against a rotating piece of glass in the middle of which a plunger was sunk (Figure 9). This technique did not spread, however, in contrast to *sagging* with which the mass production of vessels began in the first century BCE [1, 13]. With this simple technique, a straight, flat-sided tool pressed a sagging gob or disk of hot viscous glass against a convex mold placed on a turntable, creating at the same time the rim of the bowl. Probably made of baked clay, the mold was reusable, just requiring the finished vessel to be lifted off before annealing and consecutive glass

shrinkage. Mosaic glass bowls [1, 13, 19] required working with a preformed disk composed of mosaic glass slices or *florets* fused together like the parallel striped *reticella* bowls [13, 19]. Before the sagging stage, such disks had to be heated at relatively low temperatures to avoid distortion of the fused patterns during sagging.

Small bulbous bottles predating the discovery of inflation were composed of bands of colored glass or, occasionally, of gold foil sandwiched in between two glass layers [13, 19]. As in mosaic glass bowls, the bands extended through the thickness of the wall continuing on the bottom of the bottles without a seam (Figure 10). The trick could have been to let a preformed glass bowl sag vertically under its own weight over a raised support [6, 10]. Pressing the free-hanging glass toward the stake supporting a plaster mold would have created the neck. Depending on the

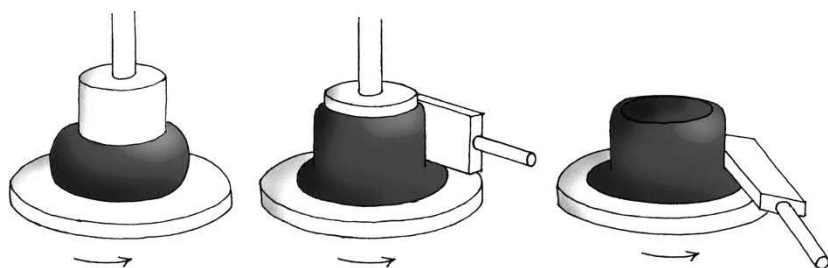


Figure 9 Making a Cretan *pyxis*: cylindrical plunger pressed into a gob of hot glass placed on a turntable; moist wooden paddle then raising the displaced glass by pressing it against the plunger; and final of the flattening the vessel's foot. *Source:* After [10].

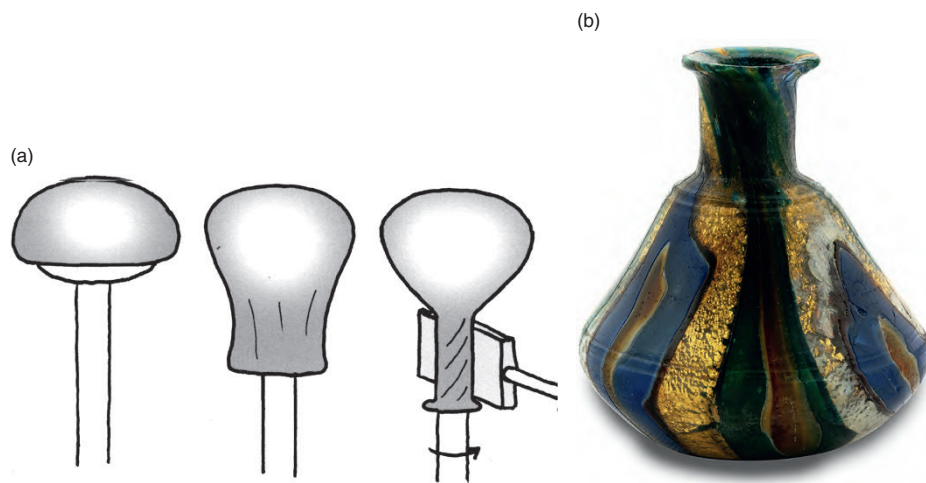


Figure 10 Making of a bulbous *colorband* bottle: preheated colorband disk or bowl flowing down and contracting on a raised plaster mold, while the neck is shaped with a moist wooden paddle pressing the glass against a turning stake. *Source:* After [10]. *Goldband* bottle (height 6 cm, maximum diameter 5.8 cm). Early first century Split (Croatia), Archeological Museum, inv. no. AMS-G-87. *Source:* Photo T. Seser, courtesy the Museum.

shape of the mold, the colorband bottles had bulbous or straight sides.

Glass vessels with angular, often carinated profiles reminiscent of contemporary pottery and metal shapes were popular as fine tableware during the early Roman Empire (c. 25 BCE–50 CE) [13]. They were produced in attractive, usually translucent colors, opaque red, and mosaic glass. But it is not yet known whether they were mold-formed, pressed with a counter mold, and finished by polishing, or rotary pressed.

Far from Italy, seamless glass bangles were a Celtic specialty relying on the enlarging of a bead. The bead was mounted either on a rod-shaped mandril and widened through stretching with a second tool or on a mandril shaped as a cone and widened by centrifugal force.

4 The Slow Blowing Revolution

4.1 A Late Invention

Like other major advances, the discovery that hot air expands heat-softened glass was probably accidental at a time when the wealth of techniques already available was not a strong incentive to invent a completely new

one. Keen observers not only noticed this original feature but were curious enough to take unknowingly advantage of the fact that, in modern physical jargon, molten silicates are Newtonian liquids that can thus deform under very small stresses (Chapter 4.1). At the relevant viscosities, this is why the glassblower could combine the pressure of the breath with gravitational and centrifugal forces to shape glass in especially complex ways with the help of simple tools and the marver [1]. For the earliest blow vessels, the weight was lower than 100 g, with values generally in the lower 7–20 g range.

The earliest archeological evidence for inflation comes from the waste of a Jerusalem workshop active in the mid first BCE or slightly later. The finds include glass tubes pinched closed at their lower end and inflated through their upper end, of which the edge was pulled outward to create a rim (Figure 11) [23]. Glass tubes, made by drawing a hollow bit of hot glass from a metal working rod, were common because chopping them up was a simple way to create beads with a thread hole.

That the earliest inflated glass happened to be a tube was crucial for the development of blowing and the blow-pipe [9]. But more than 100 years of experiments, discoveries, inventions, and improvements separated the first inflated glass tubes from full-fledged Roman glassblowing



Figure 11 Fragments of inflated tubes from a first century BCE Jerusalem workshop: fire-closed inflated bulbous ends, necks, and pulled-out rims. White and black bars: 1 cm. Source: After [22].

in the second half of the first century CE. The introduction of the iron blowpipe, the construction of a new type of glassworking furnace with a horizontal, closed heat chamber, the use of hot molten glass, and the pontil technique for fire-finishing the rim of the vessel were the most important steps in this development [4, 9]. Most, but not all of the tools now taken for granted as integral to the craft were invented during this period.

4.2 Blowing: Pipe and Pontil

As they had done previously with a solid metal rod, the earliest glassblowers throughout the Roman Empire gathered preheated chunks of glass at the tip of the blowpipe, a practice that was still common when blown mosaic glass was produced in the late first to early third centuries (Figure 2) [24]. In the beginning, the glassblowers took care not to let the glass get too hot because it might have dripped off the pipe and be wasted. When they learned how to gather a gob of hot drippy glass, the glassblowers cooled it immediately, either by gentle rotation of the blowpipe or by rolling on the marver. Only after cooling the outer skin could the glass be blown. The rims of early vessels were often ground after annealing or simply left unworked. For finishing the rim, the vessel was held with a clamp, or the artisan blew a bubble of glass on a second blowpipe against the vessel's underside while it was still on the blowpipe [4]. The pipe with the bubble was a precursor of the pontil and the bubble itself became the vessel's base after cracking off.

Invented at an as yet undetermined date in the second half of the first century, the pontil technique was the last major step in the development of glassblowing since it allowed the mouth of a vessel to be shaped while the piece was firmly held by its opposite end (Figure 12). The pontil

was a solid rod. It was attached to the bottom of the vessel with a small wad of hot glass and usually left a scar in the form of gashes or adhesions of glass, which were not removed. The circular form of the earliest scars suggests that the glass remaining on the blowpipe after cracking off the vessel was reheated and the blowpipe itself served as a pontil [4].

4.3 Mold Blowing

To combine blowing with molding was an obvious further step. Three main types of molds were designed, each with its own specific use and purpose. Mold blowing began as a technique to give vessels a surface decoration in relief that could vie with that of chased silver. While free or "offhand" blowing was being perfected in Italy, glassblowers on the Syro-Palestinian coast explored the intricacies of the multipart mold, which determined the size, shape, and decoration of the object [19]. As time went on, the construction became simpler with fewer mold parts. By the second half of the first century, many molds in Italy had just two [9].

Another type of mold, developed in Italy around the middle of the first century, was the box mold, made of stone or terracotta, with four or more smooth walls, that speeded up mass production of prismatic bottles and jars and had the additional economic advantage of not requiring the help of an assistant since the molds did not need to be opened and closed. The vessels' prismatic shapes facilitated packing in wooden boxes, while the base molding enabled recognition of the mold maker, the container, or the content. The realization that mold-blown vessels could be mass produced was probably one of the reasons for the significant drop in production of mold-blown decorated vessels in the third quarter of the first century.



Figure 12 Pontil attachment on a newly blown glass. Source: Photo Arz.



Figure 13 Replica of five-part mold for a beaker, showing mythological scenes. *Source:* Carving and photo by David Hill.

Multipart molds were usually made of terracotta clay and provided with a series of matching bosses and cavities to ensure they fit together as closely as possible (Figure 13). No such ancient mold has been identified beyond doubt, but the number of their parts is revealed by the seams left by the glass that seeped in between [9]. The mold (Figure 14) had to be open to admit the parison, but then it had to be quickly closed and opened again to release the piece without damaging the decoration, which usually had undercuts. The mold was held firm by an assistant while the glass itself was blown rapidly to avoid thermal shock. Necks and rims were usually free blown afterward [8, 9, 19, 25]. The surface of some early Roman mold-blown vessels suggests they were blown into metal molds [8, 9], as was a distinct group of pilgrim vessels decorated with Christian and Jewish symbols produced near Jerusalem in the late sixth and early seventh centuries [9, 19].

Decorative mold blowing experienced a revival in the fourth century with the invention of the *dip* mold to decorate the base and walls of free blown vessels with an attractively ribbed surface pattern [8]. These delicate vessels evoked the luxury of fine-fluted silverware without the odium of mass production, because after exiting the mold, each piece was shaped individually to yield effects comparable to *optic blowing*. The difference was that both the exterior and the interior of the vessel had ribs [19].

Dip molds were always open at the top. They owe their name to the fact that the blower simply dipped the parison on the pipe into them and blew. After lifting the glass out of the mold, the blower could twist the vertical ribs into spirals and even reinsert the piece into the mold to create the basketry patterns seen on some late vessels from the Eastern Mediterranean (Figure 15). Decorated glass cups, tumblers, and bowls blown into shallow dip molds, with a design carved into the bottom, were a specialty of northwest Europe. The central medallion frequently featured a Greek cross or a Christogram surrounded by stylized vines, baskets, birds, wreaths, palm fronds, and trees. One preserved mold is made of limestone. Upon extraction from the mold, the relief decoration was often blurred and farther disfigured by a pontil scar. In spite of the Christian symbolism, most of the vessels were used as secular, domestic tableware [26].

5 Decoration

Shapes and decorative techniques initially imitated contemporary pottery, stone, and metal until it was discovered that glass made new types of decoration possible through controlled manipulation and/or expansion of ornaments applied to the surface, and the use of colored

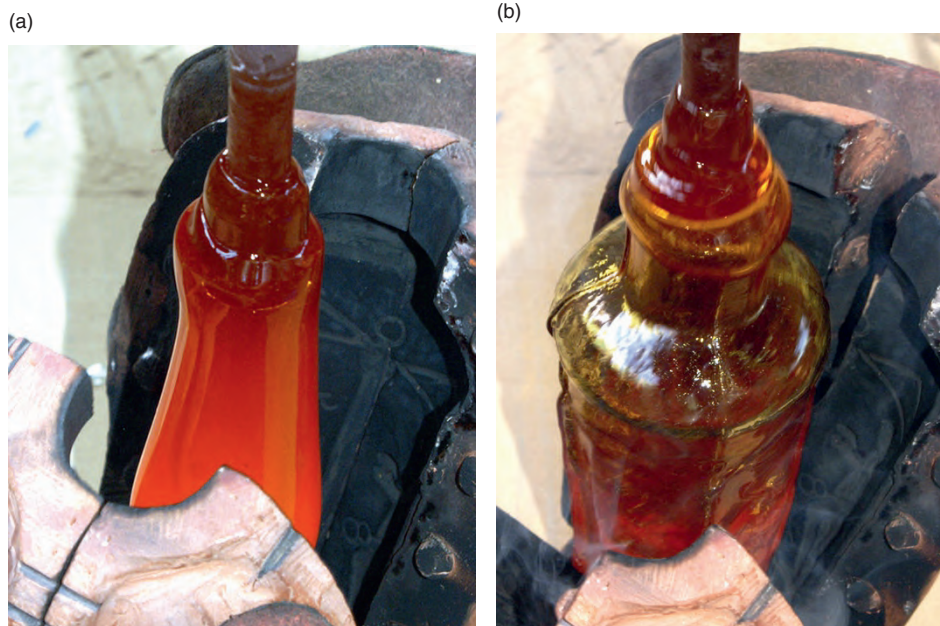


Figure 14 Mold blowing: loading of the parison in the sooted, five-part mold of Figure 13 and recovery of the mold-blown flask whose seams are clearly visible. Source: Photos Arz.



Figure 15 The basketry pattern of a cylindrical jug (height 21 cm). Syro-Palestinian production of the end of fourth to mid fifth centuries. Stuttgart, Landesmuseum Württemberg, inv. Arch 03/W148. Formerly Ernesto Wolf Collection.

glass. *Hot* decorative techniques involved the application of trails and bits of glass to the vessels' wall as well as pinching, nicking, poking, and twisting the applied ornament or even the wall itself. Colored trails and crushed glass applied before blowing could be manipulated to create marbled patterns that imitated precious stone, whereas threads in relief or prefabricated designs made of trails nicked with a specialized tool were welded after full inflation to prevent them from melting back into the wall. Early on, the *zarte Rippenschale* combined spirally wound trails with thin ribs pinched before full inflation of the parison.

Cold decoration involved faceting, engraving, and painting. Either by hand or with the aid of a rotary tool, grinding and polishing with water and an abrasive were the earliest methods used to modify glass surfaces as shown by the linear patterns present on the undersides of fourth century BCE colorless glass bowls imitating the decoration of contemporary metal vessels. Many sagged and ribbed bowls were decorated on the interior, below the rim, and/or lower down on the body, with horizontal grooves which looked like molded ridges when seen through the glass walls. The exterior of the rims of ribbed bowls was frequently ground to remove toolmarks.

After the invention of glassblowing, cut decoration became common, especially on vessels and objects made of colorless glass. Its practice was tricky, however, if the glass had not been properly annealed. Facet cutting was

an Italian innovation, which predated the eruption of Vesuvius in 79. Round, oval, and non-touching deep facets were the hallmark of early Roman cast colorless fine dishes and plates of the first and the early second centuries. Their optical illusion of evoking raised knobs in transmitted light was probably discovered when the interior of clear vessels was decorated with horizontal grooves that looked like moldings. In contrast, close-set, shallow circular or oval facets cut into the exterior surface of glass beakers, cups, and bowls were meant to be seen with reflected light, each facet reflecting it differently to create a dazzling shimmer. In the second century, cutters began to arrange the facets in horizontal zones divided by linear grooves, which was often less labor intensive than covering the entire surface with facets and facilitated the creation of more complex designs. Like facets, engraving showed up best on colorless, transparent pieces so that the technique was most common when this type of glass was in fashion. Some vessels were cut or abraded by a stone or a fine metal wheel whereas others were incised free hand, probably with a flint or possibly a diamond point. Many engravers used more than one technique on a single vessel.

Sophisticated cold work, such as painting and figural engraving, probably was executed by specialized artisans. But very little is known about their relationships with the glassblowers, the organization of the trade in blanks, or the role of patrons. As was true in other trades, glass engravers probably relied on model books. Differences in cutting techniques and cutting styles suggest that glass engravers had a firsthand knowledge of three-dimensional models, perhaps through plaster casts. Free-hand engraving with linear shading imitated the darkened outlines of paintings and mosaics. Dulled, abraded areas created color effects and the cutting of glass in *intaglio* recalled the raised relief of metal. Egypt, Rome, and the Rhineland were home to some of the most prestigious workshops. Reflecting the Christianization of the empire, several workshops added Christian subjects to their repertoires in the second quarter of the fourth century.

6 Special Techniques

6.1 Hellenistic and Roman Gold Glass

The most luxurious glasses of antiquity have long puzzled researchers. The earliest are double-walled gold glass vessels first made in the Hellenistic period and again in the “Roman” fourth century, but in a totally different way. In the former (Figure 16), the technique for cutting and applying the floral gold foil decoration closely resembles the Japanese *kirikane*, which is eminently appropriate for ornamental motifs [27]. The elegant floral patterns



Figure 16 Hellenistic sandwich gold glass bowl (height 10.7 cm, rim diameter 24.7 cm), mid third century BCE. Source: British Museum 1871,0518.2, © The Trustees of the British Museum.

sandwiched between two close-fitting colorless glass bowls were remarkable for their lack of cracks, an indication that the gold foil was not subjected to excessive heat. If the two glass bowls were formed by rotary pressing, three moist wooden plungers would have been needed: two larger ones of the same size for the outer bowl and the gold foil pattern, and a third, slightly smaller one, for the inner bowl (Figure 17) [10].

The late Roman gold glasses served a different purpose. They were not extravagant gifts for the happy few, but often became grave markers in catacombs after having been crudely chipped to shape. They depicted Christian, Jewish, pagan and mythological themes, married couples, portraits, animals and secular events like horse races, and often bear Latin mottos wishing their owners to prosper (*vivere*) or drink well (*bibere*). In most designs and mottos, the gold foil of the figural scene and inscriptions was applied onto the surface of the cold glass with water or a light adhesive [19]. The bowl and the foot were blown separately. To prevent thermal shock, the part of the bowl bearing the decoration needed to be reheated before the glassblower blew and shaped a second bubble (the bowl or the foot) and fused it hot to the part bearing the decoration. As a result, the gold foil was always full of tiny crisscross cracks.

6.2 Cameo Glass

As exemplified by the famous Portland vase in the British Museum (Figure 18), cameo vessels were usually blue and decorated with opaque white relief. It is generally claimed

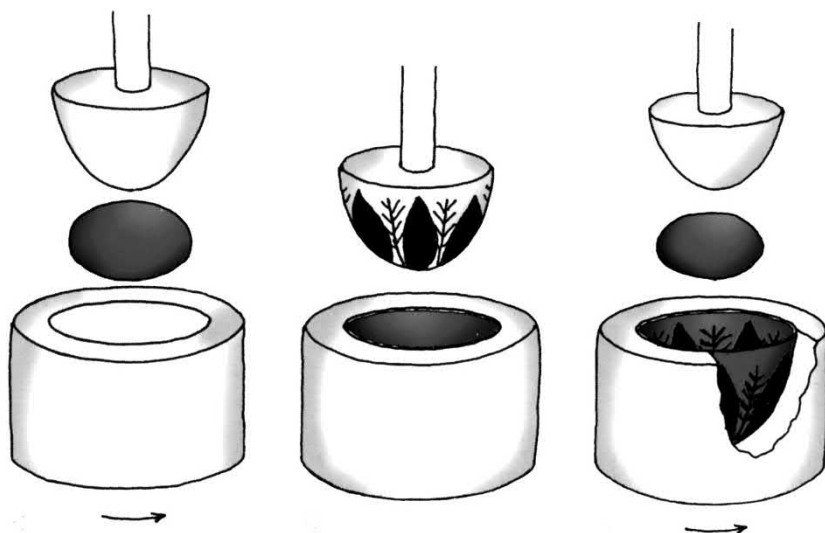


Figure 17 Three-step making of *gold glass*: pressing of the gob of the outer bowl in the mold, deposition of the gold-foil pattern adhering to a plunger of the same size, and pressing of the gob of the inner bowl with a slightly smaller plunger. *Source:* After [10].



Figure 18 Cameo glass: the Portland vase (height 24.5 cm, maximum body diameter 17.7 cm, weight 1.306 kg). Late first century BCE. *Source:* British Museum 1945,0927.1, © The Trustees of the British Museum.

that the molded white decoration was carved from bicolored blanks [28]. Some of these vessels are very large and heavy, however, and date from the very beginning of blowing when the new vessels were tiny and light weight. In addition, the pontil technique, which played a basic role in the production of blown blanks, had not yet been invented and the cross-cutting shears needed for creating the rims were also unknown. The presence of rotary scratches and the fact that the decorative relief never extends beyond the shoulders of Cameo vessels rather point to a first step of rotary mold pressing in a decorated plaster mold (Figure 19). First, the cavities for the decoration were filled with powdered opaque white glass. A drop of water held the powder together until it was dried. Then the hot blue glass was rotary pressed into the mold, melting with its heat the white glass. For a higher relief, powdered glass could be sintered in the plaster mold before rotary pressing of the hot blue glass.

6.3 Cage Cups

The *diatrete* (cage cups) are probably the most outstanding pieces of glass ever produced (Figure 20). Their decoration consisted of figural or network patterns. The earliest true cage cup is figural and dates from the late third century [29], preceding the network cage cups made

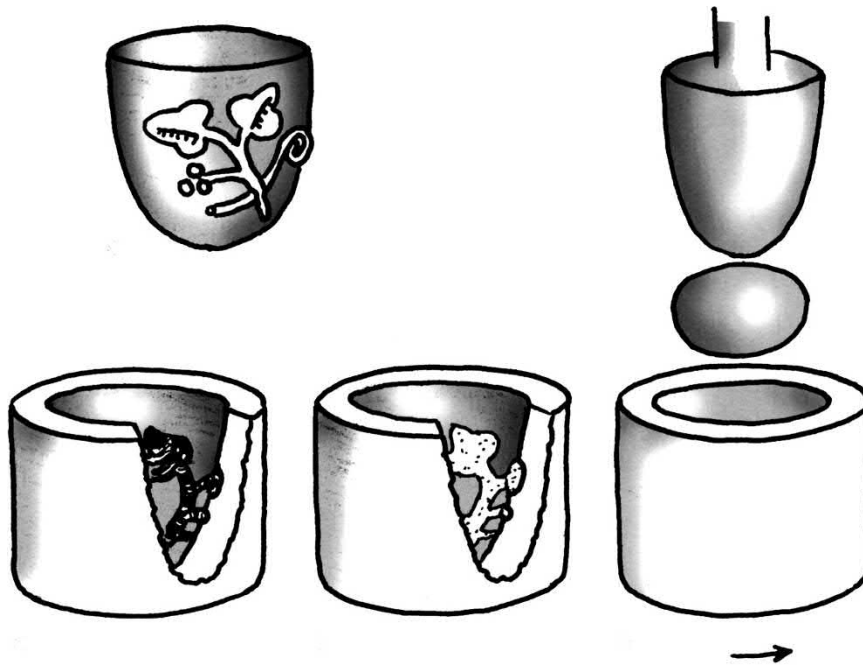


Figure 19 Two step-making of a cameo glass: model of wax or clay serving for the hollowed out interior decoration of a plaster mold, whose cavities are then filled with powdered white glass before pressing of hot blue glass into the mold with a plunger. Source: After [10].



Figure 20 Diatrete, Cage cup (preserved height 12.1 cm, rim diameter 10.1 cm). Köln, Römisch-Germanisches Museum 60.1. Source: Photo Cornelius Steckner, courtesy the Museum.

from the fourth century. Similarities with high-relief glass suggest that the earliest precursors might have been produced in a workshop specialized in high relief. The figures are often undercut so that many details stand free from the background [29], in imitation of contemporary *repoussé* silver vessels.

Carving of thick-walled blanks would have been a possibility because the water mill, indispensable for supplying energy to the cutting tools, had become common throughout the Roman Empire by the fourth century [22]. However, in addition to extremely severe breakage and cracking problems, the time spent on cutting and polishing would have been considerable. A much quicker and safer alternative [6, 30] is to assume that one made cage cups by pressing a double-walled blank on a turning wheel (Figure 21). After pressing the first gob of hot molten glass into the mold (the future cage), the glassblower inserted a smaller, perforated plaster mold into the hot glass and used a smaller plunger to press a second gob of hot glass into the mold to form the main body and to force at the same time some glass through the perforations. The tiny bridges connecting the cage to the inside bowl thus became integral parts of the main body as actually observed, although occasionally the two glasses meet somewhere along the bridge if some of the glass from the outer bowl (the future cage) was forced back into the perforations when the inside bowl was pressed.

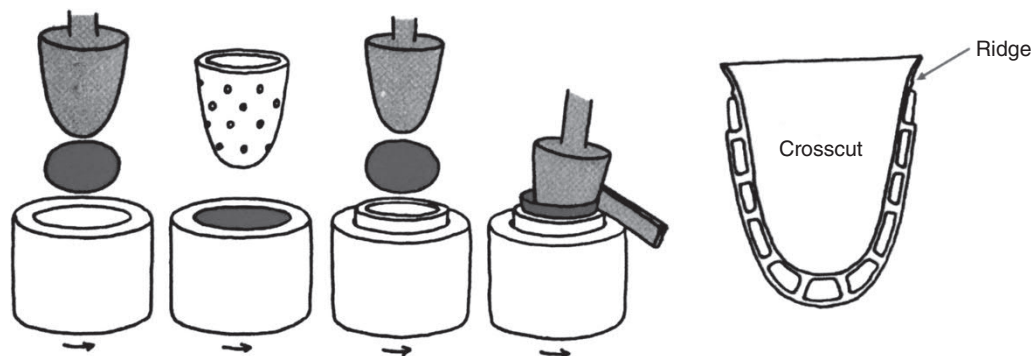


Figure 21 Four-step making of a double-walled blank for subsequent cutting of a diatrete: pressing of a first gob for the outer bowl of the network cage, insertion of a perforated plaster mold, pressing of a second gob for the inner cup and the bridges through the plaster mold, and creation of a ridge while the rim is shaped. Cross section of the double-walled blank with the perforated plaster cup still inside also shown. *Source:* After [6].

7 Secondary Glassworking

7.1 Workshops

In antiquity, glass *making* and *working* remained two separate crafts, each with its own pyrotechnology and ancillary techniques. Unlike primary production (Chapter 10.3), the shaping of glass was not bound to a specific location. Secondary workshops could be located near primary workshops, as in Israel and Egypt, but all they needed was a supply of raw glass which could come from afar (Chapter 10.3). How this trade was organized is not clear, but ingots, chunks, and even cullet found in ancient shipwrecks point to transport by sea, frequently as inexpensive ballast. Textual evidence indicates that recycling became an important source of supplies from about 70 CE on [4, 31].

Secondary glass workshops were located either on the edge of town in northwest Europe (to minimize the risk of fire) or more centrally in the Eastern Mediterranean. At Bet She'an (Israel), a downtown workshop destroyed by a sixth to early seventh century earthquake had a courtyard and two connecting rooms showing traces of shelves for storing glass vessels [32]. Most of the vessels were kept in the front room, where the furnace was located next to the wall of the doorway, surrounded by moils or crack-offs from the blowpipe, knock-offs from the pontil, and glass drops. On either side of the furnace, blown vessels and olive pits (known for their heat-storing properties) were found in heaps of black ash, which probably served as rudimentary annealing lehrs. Piles of glass chunks lay ready for use. The storeroom contained additional shelves of vessels, sacks filled with cullet, and a large jar full of chunks of raw glass.

7.2 Furnaces

Some Roman oil lamps depict a worker blowing a tall-necked bottle while sitting on a low stool in front of a marver depicted as a small ledge protruding from the furnace (Figure 2, Chapter 10.4). The piece attached to the blowpipe could be entered horizontally into the furnace's upper compartment through the working port at the center. The lower compartment served for stoking. The rectangular blocks on the floor in front of the furnace were probably blocks of raw glass waiting to be used, but what the squatting man was doing on the left is unclear.

With respect to the core-forming furnace, the most significant change was the closed, horizontal heat chamber. It allowed not only higher temperatures to be reached but also ensured that the glass heated evenly on all sides, which was crucial for expanding evenly during inflation. The new glassblower's furnace was thus a revolutionary invention. It had one major disadvantage, however, which persists today: because the artisan cannot shape the glass and simultaneously control its temperature, all the shaping has to be done outside the furnace in between successive reheating steps. The basic distinction made between *short* and *long* glasses (Chapter 4.1) is thus a direct consequence of the invention of the glassblower furnace.

The remains of the lower structures of these furnaces have been found all over Europe. The majority are circular, with an inner diameter of about 45–70 cm. Pots for remelting raw glass were rare before the third century, but common later on. Tank furnaces have been assumed to exist as early as the mid first century because glass dripings were observed on their floors, but no pots were found [33]. It has been argued, however, that tank furnaces did not become common until the third quarter

of the first century, when polychrome vessels went out of fashion and blowers began to use mostly natural bluish green glass [34]. This meant that one color of molten hot glass sufficed. As observed at other mid first century furnaces [35], the drippings on the floor resulted from small chunks of raw glass that got too hot and melted when they were picked up on the tip of the blowpipe.

7.3 Tools

Neither the commonly held opinion that ancient blowpipes were made of iron from the beginning, nor the hypothesis that ceramic blowpipes were used at an intermediate stage [1] can be proved or disproved at this moment. The earliest evidence for the use of iron blowpipes is the presence of oxidized iron in mid first century waste glass, originating from the *crack-offs* remaining attached to the blowpipe after separation of a completed vessel [35].

In addition to the blowpipe and the pontil, the U-shaped iron shears with parallel blades were the most important glassblower's tool of antiquity. Originally a Celtic invention, this *forfex* was the universal cutting tool of the Greco-Roman world, thanks to the springy blades that opened automatically when not pressed together (Figure 2, Chapter 10.9). The tool could not cut hot viscous glass, however, which is why Roman glassblowers usually began the handle of a vessel at the shoulder, pulled the glass up, and attached it at the upper end where they drew the extra glass out thin and snapped it off. Often they folded the extra glass back and forth to create interesting folds and spurs at the upper end of the handle [19]. For most ancient glassblowing techniques, these simple iron tools sufficed along with a wooden board for shaping and a wooden stick for widening rims. An interesting feature seen on many Roman blown vessels is the fire-polished rim that resulted from the wooden stick catching fire through contact with the hot glass. When shaping was completed, a gentle tap on the pontil let the piece slide onto a wedge-shaped branch to be deposited for annealing.

7.4 Blowers

Unlike pottery, glassblowing did not develop into a large-scale enterprise in antiquity. The Roman glassblower furnace was small, imposing physical restrictions on the number of persons who could work simultaneously [4, 34, 35]. Nevertheless, a glassblower could have averaged 100 vessels per day or 330 000 in 30 years. That such a long period of activity may have been possible is

suggested by the tombstone of the *opifex artis vitriae* Julius Alexsander who died in Lyons at age 75 [4, 31].

Little is known about the financial and social position of glassblowers although quite a few names are known. Ennion, who specialized in fine mold-blown tableware, stood out above all others in the first century eastern Mediterranean. The addition of *the Cypriot* or *from Sidon* in signatures found on mold- and free blown tableware, respectively [9, 31], suggests that others too moved through the Roman Empire as did Julius Alexsander, who was born in Africa. As for the aforementioned Roman oil lamps (Chapter 10.7, Figure 4), the names of the glassblowers added on one of them may indicate that they were Athenian *liberti* (freemen) working in Italy [4].

According to papyri, legal documents and epigraphic sources, glassworkers in Egypt were regarded as a group for tax purposes in the early first century and as a guild in the fourth [4, 31]. Elsewhere, artisans appear to have been independent entrepreneurs probably leasing their facilities as did potters [4, 31]. If clearance on exit had been a general condition in leases, that would explain the existence of large deposits of waste glass and cullet buried in pits as found in glass workshops at Saintes (France), London, and Nijmegen (The Netherlands) [31].

In antiquity, women were active in beadmaking and glassblowing. Also known as Didyme, a Sarapodora is mentioned in a mid third century contract along with two male glassworkers from Koptos [36]. Female names are also found in basemarks on the undersides of square bottles [37]. Sentia Secunda (late first to early second centuries) added the information that she made VITR (*vitrum* or *vitra*) glass (or glass vessels) at Aquileia (Italy).

The price of glass varied depending on the kind of production. Raw glass and smooth (i.e. undecorated) glass vessels were sold by the pound. According to the Edict of Maximum Prices issued in 301 by the emperor Diocletian (r. 284–305), the 25 *denarii* daily wage of an unskilled laborer would have bought one or two vessels of *Judaeian* (naturally colored bluish green) glass or one vessel of *Alexandrian* (colorless) glass of average size. Even though these prices were 10–20 times higher than that of an equivalent pottery vessel, they were probably lower than the production cost of Judaeian glass [4, 38]. As for window glass (Chapter 10.8), the maximum price was 8 or 6 *denarii* per pound depending on quality. A 25 × 25 cm window pane would have weighed about 2.2 Roman pounds and cost 17.6 or 13.2 *denarii* for the best and lower qualities, respectively [38]. As the main function of window panes was to bring in light without losing warmth [39], glazing did not require the same quality as vessels, which is why the former glass was much less expensive than the latter [38].

8 A Short Retrospective Overview

8.1 The Spread of Glass

Vitreous materials had been around for more than a millennium before true glass was made on a regular basis, from c. 1550 BCE onward (Chapter 10.2). Because the new material did not prove indispensable for any specific function, it owed its initial success to the brightness of its rich colors, which surpassed those of natural stones and the glow of faience. Glass was used first as beads, jewelry, and decorative inlays in furniture, boxes, and coffins, and even in architectural context as wall decoration [13], then as colorful core-formed vessels. As an intermediate production step, colorless and natural bluish green colored glass was not valued as such [5].

Clear colorless glass, purposely decolorized with antimony (and in later periods often with manganese), made its first appearance at Gordion (Phrygia) in the eighth to seventh centuries BCE. Wide, shallow bowls were decorated with a petal motif that was convex on the exterior and concave on the interior in imitation of metal vessels. The fashion was revived in the late fifth to fourth centuries BCE with bowls that were usually smooth on the interior. The glass itself obviously imitated rock crystal, with which such shapes would have been difficult to create because of polishing difficulties and of the risk of disfigurement or breakage caused by a small mishap.

The ease of shaping glass led to several new applications of transparent glass in the Roman period. Again its acceptance began much earlier as a *thing of beauty* reserved at first for temples as dedications to the gods and for luxury items such as jewelry. From the mid fourth century BCE colorless glass vessels began to grace the tables of the wealthy [20]. In Greece, the optic qualities of clear colorless glass were a source of fascination from the moment it became available. In addition, transparent glass played a role in the construction of mechanical devices and gadgets and especially in the beginnings of optical studies (Chapter 10.10).

It is usually thought that the invention of glassblowing revolutionized the ancient glass industry because vessels could be made much faster. However, it was taking longer to blow a ribbed bowl than to make one by tooling on a turntable. The first mass-produced glass vessels, Hellenistic grooved and sagged bowls, predated the first blown vessels, as did ribbed bowls, which were still being sold in Herculaneum at the time of the Vesuvius eruption in 79 when blown drinking vessels had ousted pottery thanks to their already well-known advantages.

Blowing enlarged the existing repertoire of vessels with a wide range of shapes so that the use of glass in households increased greatly during the first century CE. Much

of it was blown, but blown luxury wares were nonetheless rare before the introduction of the pontil. Glass lamps became common from the fourth century onward [4] especially in Italy and the Eastern Mediterranean. However, it was for windows that transparent glass had the most impact in antiquity (Chapters 10.3 and 10.8), and it was during the Roman Empire that wall and floor mosaics made of colored glass cubes became common in private villas and public buildings.

8.2 The Slow Rise of Glass Blowing

After the discovery of inflation in the eastern Mediterranean, it took at least one century until the novel blowing technique spread widely, even to western Europe, after it had been perfected in Italy. As usual, older materials, techniques, and concepts survived for a considerable time. The first successful innovation in glassworking had been core-forming, which transformed a ceramic technology into a widely accepted technique of glassworking. Primarily (but not exclusively) a means for the production of attractively colored bottles, core-forming was so successful that it remained in use for 1500 years. The earliest blown vessels were small glass bottles, commonly called *unguentaria* or *balsamaria*. By far the easiest and most simple shape to produce with the novel technique, many bottles were blown in attractive transparent colors. Even more bottles were blown from natural bluish green glass, which was less expensive. These bottles were much lighter than their core-formed equivalents, not a negligible factor in an economy where glass vessels were sold by weight. In addition, blowing was considerably faster than forming around a core that had to be scraped out laboriously and left an uneven surface that contaminated the interior and hampered reuse. The invention of glassblowing caused the death of core-forming.

The new blown bottles fulfilled a real need as containers for medicinal preparations. Thousands of *unguentaria* have come to light all over the Roman Empire in civil and funerary contexts. Glassblowers soon enlarged their repertoire with bottles, jugs, and jars, which were difficult to produce by rotary pressing because the diameters of their neck and/or rim were smaller than their maximum diameters. Rotary-mold pressing was nonetheless the most serious rival of glassblowing. Like core-forming, it stemmed from ceramic technology, but it gave rise to many other techniques predating blowing and took great advantage of the properties of plaster for making molds. Thus, innovation was slow with respect to fine glass tableware, especially for open shapes with a rim diameter equal to or larger than the maximum diameter.

Throughout the first and well into the second century, rotary pressing and related older techniques remained important production methods next to blowing. Eventually, glassblowing became dominant for all vessel glass, but rotary pressing did not disappear entirely.

The development of glassblowing was hindered by the slow acceptance of the pontil technique. Many workers apparently did not trust the transfer from blowpipe to pontil when blowing large heavy pieces such as cremation urns with massive, decorative glass handles. The absence of pontil scars suggests that the glassblowers reverted to earlier techniques such as the use of a clamp to hold the vessel.

The three types of molds invented in antiquity each had a different impact and different history with respect to innovation. Decorative mold-blowing with the aid of multipart molds began in the Eastern Mediterranean during the first quarter of the first century CE as a way to emulate contemporary silver vessels decorated with *repoussé* relief [9, 40]. The technique may have been introduced into Italy in the early first century. However, unlike the small free-blown bottles, which were an immediate success, vessels blown into multipart decorated molds did not thrive in the West before the mid first century [41]. After the technique gained a foothold in Italy, the construction of the molds was simplified. Many pieces were blown into two-part molds. The introduction of box molds for the mass production of prismatic vessels caused general recognition that mold-blown decorated vessels were not individually crafted. As a result, decorative mold-blowing fell out of favor in the West [9, 40]. The box mold for blowing prismatic bottles and jars was invented in Italy around the mid first century CE or slightly later. It was an immediate success. In the eastern part of the Roman Empire, the use of box molds was never as universal as in the west.

In the late third or fourth century, glassblowers invented a technique for blowing window glass, the cylinder technique [39], which would eventually oust cast flat glass of the matt/glossy type and remain in use for the production of flat glass until the twentieth century (Chapter 10.8). In this domain, too, innovation was slow. In the east, the older technique persisted in use for some time.

The fourth century was actually an innovative period in the history of glassblowing [9]. Syrian blowers began to expand geometric surface motifs created in multipart molds by continuing to blow after exiting the mold. Expanded concentric circles were the commonest motif. Although this technique remained a regional curiosity, it pointed the way to a novel use of decorative molds that would dominate mold-blowing for all times to come, namely, the dip mold. Syro-Palestinian glassblowers used these molds to create bowls with barely expanded

honeycomb patterns, which were appreciated east and west. The real success story, however, was the vertically ribbed or fluted dip mold. Easy to make and easy to use it enabled the glassblower to produce a large variety of expanded vertical and spiral rib patterns in imitation of contemporary silverware.

9 Perspectives

The scenario of a gradual development and anchoring of ancient glassworking techniques based on rotary mold-pressing makes sense from a historical and technological viewpoint. Although experiments have demonstrated the feasibility of the proposed reconstructions, dissent among specialists is polarizing the community of glass researchers in many fields of research from art historians and archeologists to chemists, laboratory scientists, conservators, and glassblowers. With Lierke's theoretical reconstruction drawings in hand [6, 10], a new generation of glassblowers can begin to experiment and/or attempt to produce reliable replicas of ancient glass vessels. For the shaping of vessels with carinated profiles, made perhaps on a raised support, the lack of an appropriate furnace for working above and in the heat may be an issue that needs first to be resolved. The advantages and disadvantages of working glass with such furnaces have yet to be fully explored. The price of gold foil sufficiently thick for experiments to replicate Hellenistic gold glass may be an obstacle of a more prosaic kind.

Two quite different projects will finally be mentioned to illustrate the diversity of approaches followed to understand better ancient processes. The first aims at making basic information on important pieces as widely available as possible through an open-access database set up at the Römisch-Germanisches Zentralmuseum in Mainz (Germany). Its goal is to document Roman cage-cups thoroughly through high-quality photographs of both vessel and surface [42]. Hopefully, the documentation will include microphotos of the reverse of the cage and the interior wall of the cup where details such as shortened horseshoe chattermarks suggesting double-walled pressing might be detected. Launched at the initiative of the Australian National University at Canberra, the second project highlights the use of state-of-the-art techniques applied in industrial or academic glass studies (Chapters 2.1 and 2.2). Through high-resolution X-ray scanner tomography combined with a visualizing software program, the important question addressed in this case is the production of cameo-glass vessels and, in particular, the nature of the interface formed between the white and the blue glasses during the shaping process.

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10.6

Glazes and Enamels

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1 Introduction

Glass has long been highly valued in the form of thin layers termed *enamel* or *glaze* depending on whether the substrate on which it is deposited is smooth (e.g. metal and glass) or porous (e.g. porcelain). From Egypt, Phoenicia, and Mesopotamia to the Indus Valley, glazed artifacts date back to about 2000–1500 BCE [1]. There is actually evidence that bulk glass was a by-product of glazes, once the great aesthetic and practical value of the new material had been acknowledged in the Middle East (Chapter 10.2). Such coatings were used not only for decoration purposes (Figure 1) but also for tightening a porous body and hardening its surface, which made, for instance, possible to keep safely liquids or other substances in large pottery vessels. In the Western world, the first enamels date back to at least 1500 BCE in Cyprus [2] whereas an older written mention of an enameled shield is found in the *Iliad* (eighth BCE). From diverse areas, famous artifacts include an eleventh century BCE enameled bronze wine ladle from the early Western Zhou dynasty (British Museum) or numerous Celtic enamels on brass, bronze, gold, and iron made from at least the fourth BCE with blue, red, green, yellow, and black hues [3]. As to *millefiori* (1000 flowers, in Italian) enamels, they appeared in Ireland during the seventh century CE.

Since then, a great many new applications have been designed, ranging from porcelain or glass isolators coated with iron oxide-rich enamels to improve the electrical insulation of wire supports in wet atmospheres [4] to

the development of advanced ceramics such as particular dielectric passive components (e.g. capacitors, substrates, sockets) that are at the roots of the development of microprocessors and computers. Glazes are also deposited on alumina electronic substrates to be used in standard or harsh conditions [4] whereas, following a tradition originating in the glazes deposited on stone in ancient Egypt [1], enameled lava remains used in contemporary building décor.

Regardless of their functions and of the possibly complex shapes of their substrates, the deposited glass layers must not exhibit any puddle but have a constant thickness. Hence, it is obvious that enameling and glazing technologies involve much more than the preparation and firing of glass compositions. Without trying to deal with all varieties of enamels and glazes (Figures 1 and 2), this chapter will review their current preparation and the technical constraints exerted in particular by thermal expansion matching, describe the most pertinent innovations regarding composition and color, and finally present an overview of the history of enamels and glazes.

In preamble, some definitions are in order: *stoneware* designates nonporous pottery or ceramics fired at temperatures higher than 1200 °C; *fritware*, pottery in which some ground glass has been mixed with the starting clay and sand material to promote partial melting upon firing to cement the grains with the molten frit; *porcelain*, various kinds of white wares that share a common vitreous surface and a nonporous body as first made from 3000 to 1500 BCE during the Chinese Shang and Shang-Zhou dynasties (in the form of protoporcelains, which were already fired up to about 1200–1250 °C) [5]; *celadon*, a green Chinese porcelain as named in France in the seventeenth century; and *cloisonné* and *champlevé*, enamels prepared with two different kinds of techniques.

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Figure 1 A variety of glass coatings. (a) Enealed Venetian chalice (circa 1480–1500, Sèvres Cité de la Céramique Coll.); (b) Hispano-Moresque luster pottery (fifteenth century, Sèvres Cité de la Céramique Coll.); (c) glazed Ottoman Kütahya bowl (end of seventeenth century, Sèvres Cité de la Céramique Coll.); (d) Chinese cloisonné (sixteenth century, UCAD Coll.); (e) Han Viet pottery glazed with ashes (before sixth century, Private Coll.); (f) Raku tea bowl (twentieth century) voluntarily broken and restored with the golden lacquer technique (Source: Courtesy Andoche Praudel, potter, Private Coll.); diameter ~20 cm, except (e) (~12 cm) and (f) (~15 cm). Source: Photos Ph. Colomaban.

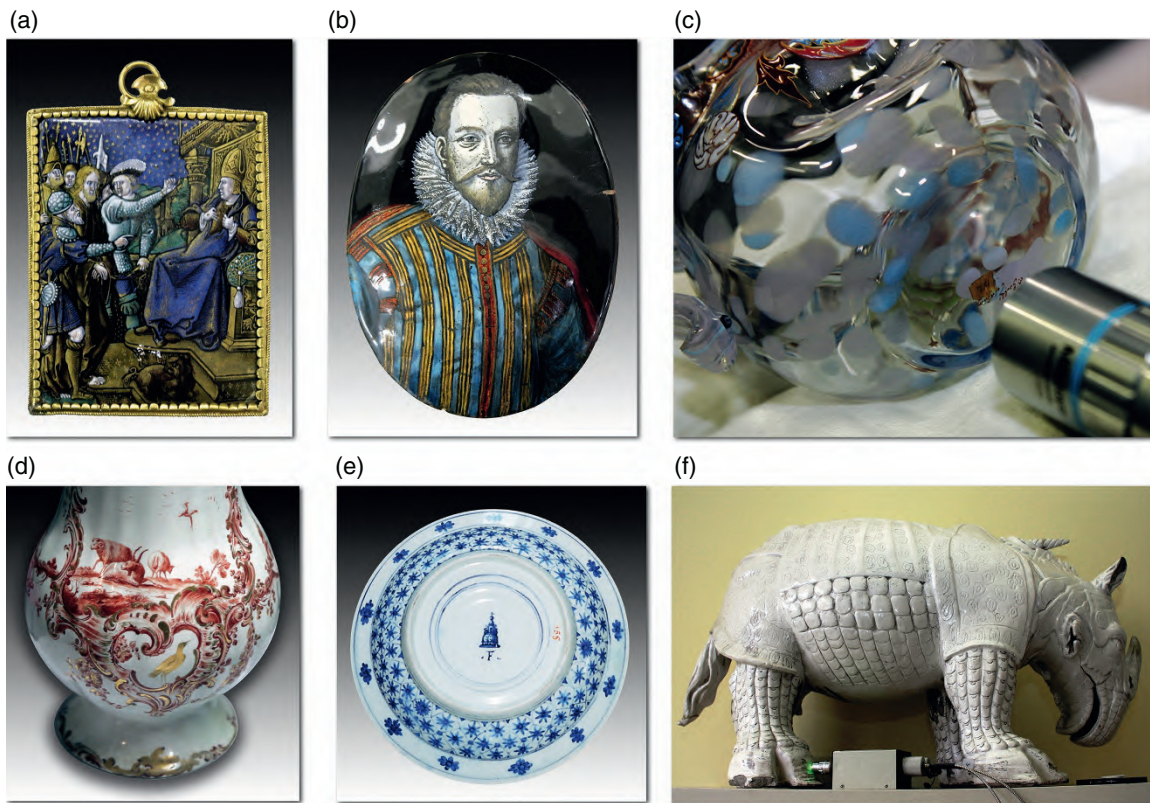


Figure 2 Limoges enamels. (a) Plaque depicting Jesus before Ponce Pilate tentatively assigned to Penicaud (sixteenth/seventeenth century, UCAD Coll., partially restored); (b) plaque depicting King Henry IV (initial seventeenth century dating, actually a nineteenth century fake; UCAD PE1640); (c) Gallé enameled glass (UCAD Coll.); (d) Sceaux porcelain were decorated with Cassius Purple enamel (Sèvres Cité de la Céramique Coll.); (e) Medici porcelain plate (sixteenth century, Sèvres Cité de la Céramique Coll.); (f) rhinoceros from Pilnitz garden (J. F. Böttger, Meissen, early eighteenth century, Sèvres Cité de la Céramique Coll.); largest dimension ~20 cm, except (a), (b) (~12 cm) and (f) (~150 cm). Source: Photos Ph. Colomaban.

2 Preparation and Thermal Constraints

Coatings, in general, are made from either glass precursors through in situ reaction and melting or with ready-to-use glass frits. An aqueous slurry is prepared from these materials if the substrate is an unfired or a porous pottery. The slurry is deposited by immersion of the object or painting with a brush or spray dried. The slurry must have the right viscosity, thixotropy, etc., which are optimized with specific additional ingredients such as clays, kaolin, or polymers and glues. If the substrate is not porous, water is replaced with organic solvents/media and glues or similar additives are incorporated. The coated items are then heated to form the glass coating and to develop a specific color and/or gloss.

The coating thickness ranges from a few tenths of microns in *salted* stoneware to a few millimeters in *celadon* and *cloisonnés*. The coating must readily melt upon firing to yield a nice gloss and join smoothly with the substrate, which requires the precursor mixture to consist of

a fine powder. Along with firing, grinding is the most energy-intensive operation in the *Arts du Feu*, which might be why mechanized grinding techniques were developed only in the Middle-Ages with water mill energy. To get fine powders, ancient craftsmen thus relied instead on the firing of plants (ashes), shells and calcareous stone (chalk), bones (ashes), and flint pebbles (silica) together with water washing to eliminate impurities. In this way, they sometimes achieved directly the right composition (Figure 1e) [6].

However, craftsmen have long known that composition is not the sole parameter that governs final quality [6–11]. For a given composition, the glaze can be matt or glossy, well coated (Figure 1c), or crawled (Figure 3c) depending on grinding time. The glaze ingredients used to be ground in a mortar or in a rotating barrel of water containing flint or quartz pebbles (now steel, alumina, or zirconia balls depending on glaze composition). Upon firing, the reaction rate increases with the initial compaction of the deposit and it also depends on temperature, duration, heating rate, particle size, volatile content, and on the reducing or oxidizing nature of the gas atmosphere.

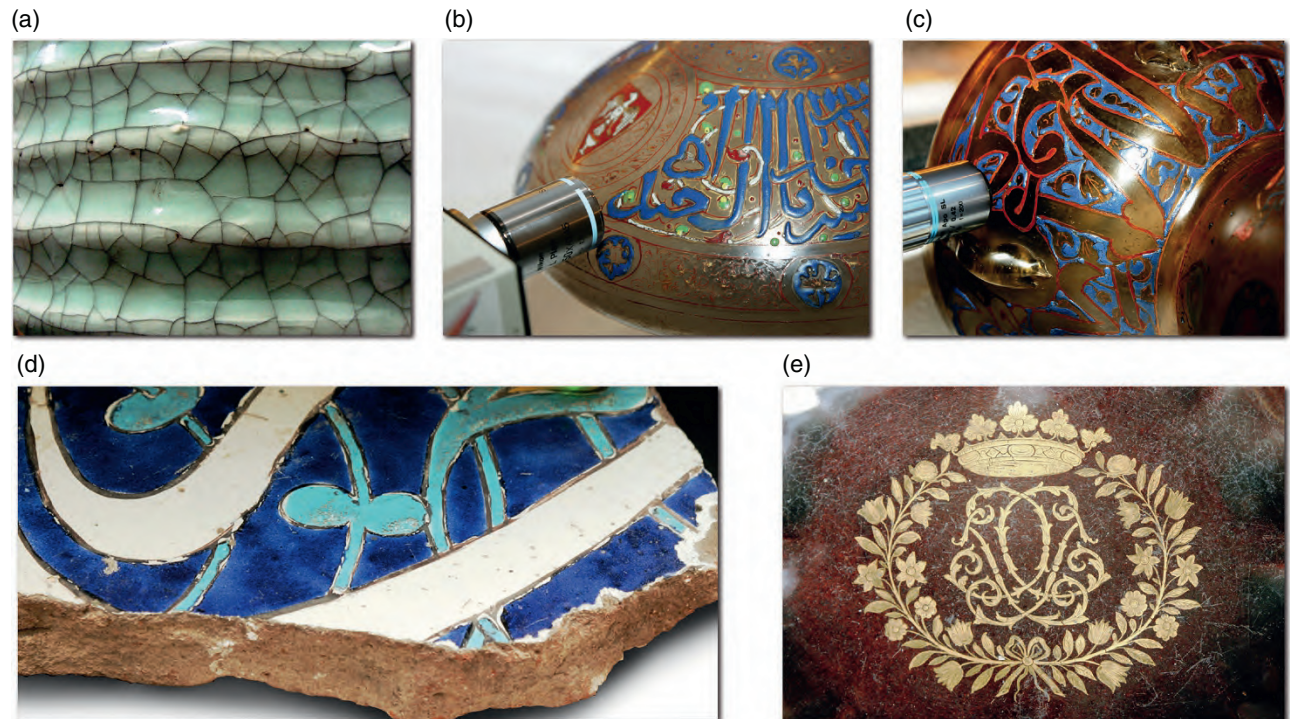


Figure 3 Firing defects on glazes and enamels. (a) Celadon cracked glaze (nineteenth century, Qing Dynasty, Private Coll., $\sim 5 \times 8 \text{ cm}^2$); (b) high-quality Mamluk enameled glass bottle (diameter: $\sim 15 \text{ cm}$), exhibiting a high-quality glossy enamel and (c) Mamluk enameled mosque lamp (diameter: $\sim 30 \text{ cm}$), where the glaze has failed to adhere to or wet the body on firing (crawling) (fourteenth century, Louvre Museum Coll.); (d) *Cuerda seca*-like technique: a line hinders the glaze to go out of the defined area (fifteenth century, Ottoman Empire, Private Coll., $\sim 4 \times 9 \text{ cm}^2$); (e) micro-crazed red glaze of a gilded Meissen Bottger stoneware (Sèvres Cité de la Céramique Coll., $\sim 4 \times 6 \text{ cm}^2$). Source: Photos Ph. Colomban.

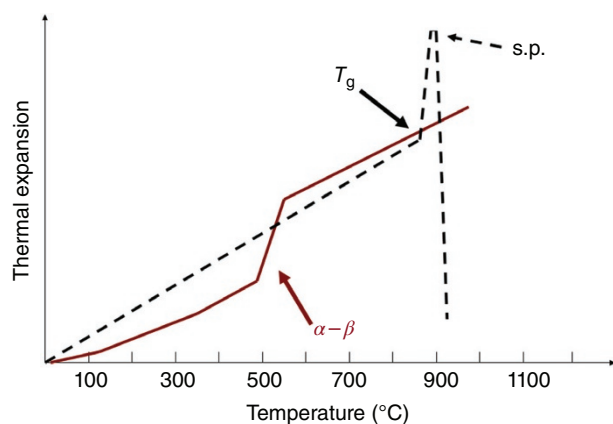


Figure 4 Control of the glaze quality: comparison between the thermal expansion of a quartz-rich ceramic body (solid line, α - β phase transition) and a glaze (dashed line; T_g : glass transition temperature; s.p.: softening point).

Because sintering is driven by atomic diffusion, longer heating times have similar effects as temperature increases or grain size decreases.

Controlling the contact angle between the melted coating and its substrate is mandatory to ensure complete wetting and also to keep the thickness constant. Bonding between the substrate and the coating is also very important. For metal substrates, a ground or under coat is generally needed to ensure adherence and accommodate the thermal expansion mismatch between upper coating and substrate [4]. Cobalt and nickel oxides were the best materials in this respect, followed by cupric, manganese, and iron oxides. Glazes for decorative purpose were then applied on the ground coat.

Coatings widely differ in composition because of the thermal-expansion match that must be achieved with a great many different substrates during the firing and cooling operations (Figure 4). Two different techniques are distinguished in this respect. With the *Grand Feu* (Great Fire), for instance, used to make porcelain, the coating and its substrate are simultaneously fired at temperatures ranging from 1200 to 1400 °C. With *Petit Feu* (Small fire), Muffle fire, or *mina'i* (in Iran), lower temperatures of 600–1000 °C suffice because the substrate has been separately fired once or twice at higher temperatures [10, 11].

In practice, the thermal expansion coefficients of metals range from 100 to $220 \times 10^{-7} \text{ K}^{-1}$ (steel, 90–180; gold, 140; brass/bronze/copper, 180–160; silver, 195; aluminum, $220 \times 10^{-7} \text{ K}^{-1}$). These coefficients are generally lower than $100 \times 10^{-7} \text{ K}^{-1}$ for ceramics (amorphous silica, 1–0; SiC, 35; mullite, 50; porcelain, 65; alumina, 75; zirconia, $105 \times 10^{-7} \text{ K}^{-1}$) and can even be negative for β spodumene/eucryptite (-10 to $-5 \times 10^{-7} \text{ K}^{-1}$, cf. Chapter 7.11).

A further complexity results from the α - β phase transition of quartz, which causes a highly anomalous expansion near 565 °C (Figure 4) for quartz-rich raw materials. As for silicate glasses, their thermal expansion coefficient increases from 30 to $80 \times 10^{-7} \text{ K}^{-1}$ from borosilicates to lead-based materials, and decrease when SiO_2 , B_2O_3 , CaO , MgO , or ZnO are substituted for Na_2O and K_2O [4, 7]. Although thermal expansion of solids is a complex phenomenon determined at the atomic level by the number of bonds per unit volume and their anharmonicity, it has long been accounted empirically with coefficients first assigned to the constituting oxides by ceramist Hermann Seger (1839–1893). Optimized calculators are now available [12].

Another important property is tensile stress. As usual, it is much smaller on tension than on compression for silicate glasses. Because of its thinness, a coating should not be put under tension but gently compressed by the substrate. The slow expansion experienced by porous ceramics with time if exposed to humidity must also be accounted for. Upon cooling below the softening point, i.e. the temperature at which the coating layer sticks on the substrate (Figure 4), the contraction of the glass coating is monitored by the thermal expansion mismatch [4]. To result in a compressive stress, the thermal expansion of the glass should be lower than that of the substrate. On the contrary, a glaze cracks when the substrate expansion is too low (Figure 3) whereas too high a compressive strength causes peeling.

The most common defects of coatings are volume bubbles, craters, and pinholes induced by gas formation, generally from the body-interface reaction when glaze and body are fired together. However, small, micron-sized bubbles are specially developed in *celadon* (Figure 3a) and opal glazes [9, 10, 13] for opacification or aesthetic effects.

3 Composition and Microstructure

3.1 Pottery Glaze

The raw materials actually used are not oxides, but mineral substances such as stones: clays, feldspars, talc, quartz, flint, or carbonates, the components to which craftsmen refer [4, 6–9, 14]. Because the compositions of these natural substances are highly variable, even within a given quarry, craftsmen mix raw materials from different places or, better, from different origins to average out differences and limit chemical fluctuations. When adjustments could not be made in the past in response to composition changes, then the quality of the production was decreasing and the factory might even disappear.

Like materials scientists, archeologists and art historians usually report glaze and enamel compositions in

Table 1 Modern porcelain glaze compositions expressed in terms of either oxide or raw materials (wt %, after [16]).

Raw materials	Oxide	NG6 glaze	NG33 glaze
	SiO ₂	63.16	73.87
	Al ₂ O ₃	17.87	14.31
	CaO	11.46	4.95
	K ₂ O	5.72	4.85
	Na ₂ O	1.37	1.16
	Fe ₂ O ₃	0.19	0.14
	TiO ₂	0.05	0.03
	MgO	0.19	0.69
Standard kaolin (ECC) ^a		8.70	7.85
Calcined kaolin (Dorkamul) ^b		13.16	8.75
Quartz (Norquartz 45) ^c		6.89	33.35
Feldspar (Norflux 45) ^c		45.67	38.45
Wollastonite FW325 (Partek) ^d		25.58	8.90
Dolomite (Microdol 1) ^e		—	2.70
Firing temperature (°C)		1340	1400

^a English China Clay (St. Austell, UK).^b Dorfner (Hischau, Germany).^c North cape Minerals (Stjernoy, Norway).^d Partek (Helsinki, Finland).^e Norwegian talc (Bergen, Norway).

terms of oxides or elements as determined from chemical analysis (Chapter 5.1, [15–17]). Potters and enamelers put the emphasis instead on raw materials, which actually determine the actual firing process relevant to their batch (Table 1). They do it by following another procedure designed by Seger who distinguished acid [SiO₂], amphoteric [Al₂O₃], and basic [flux: CaO, Na₂O, K₂O, and MgO] oxides [4, 6, 14]. The temperature, at which a liquid phase forms, a basic parameter for the reaction/bonding of the coating with the substrate, is then determined more by the particular raw materials used than by the mean chemical composition. Because the advancement of reactions (through atomic diffusion) depend on both temperature and time, Seger in addition designed reference cones made up of specific mixtures, which deforms and melts according to given controlled firing conditions (temperature and heating rate) in the wide temperature interval 500–1520 °C [12]. The interest of the procedure is apparent in Table 2 where firing temperatures range from ~600 (Cone 022) to ~1430 °C (Cone 15).

Compounds such as lead oxide are highly volatile and diffuse rapidly in the substrate, however, in which cases compositions obtained from elemental analyses slightly differ from those of the precursors. Low-firing lead-free glazes maturing at 1050 °C or less (Seger Cone #2) have one to two parts of silica per part of the other ingredients.

Higher-firing glazes melting at ~1250 °C (Cone 10) have three to five parts of silica per part of others. High-temperature fired porcelain glazes have ~10 parts or more of silica (Table 1).

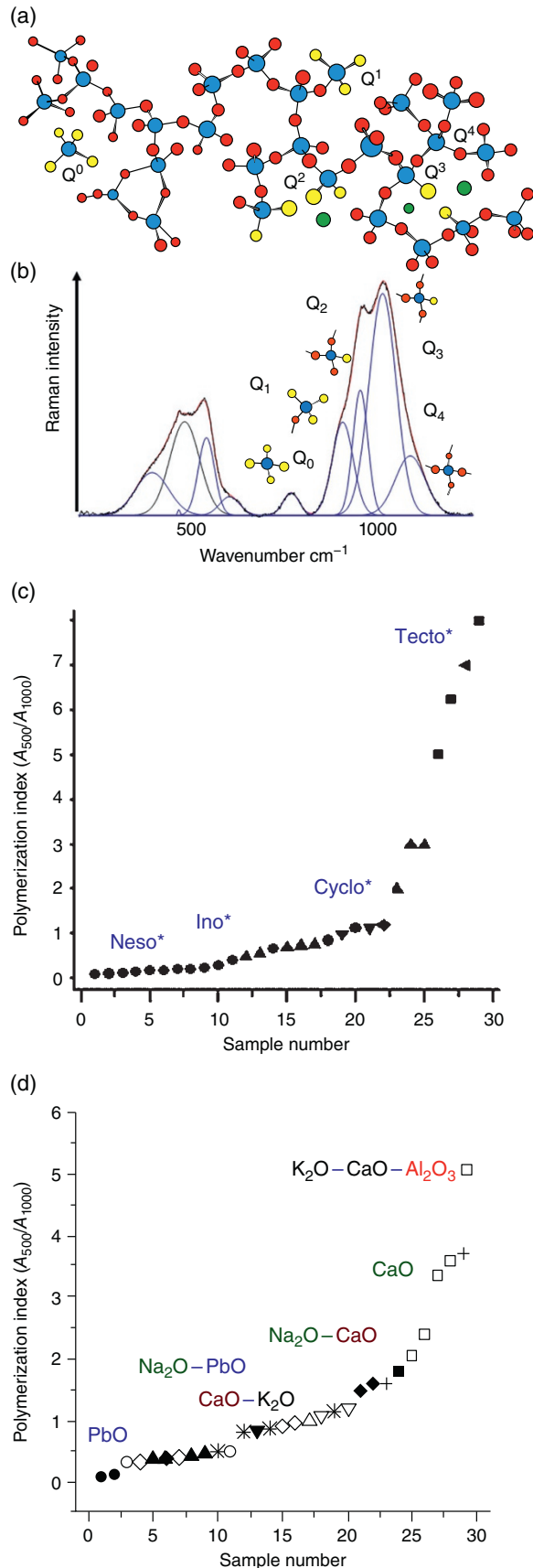
These empirical rules are now complemented by fundamental insights derived from advances made through studies of structure–composition–property relationships (cf. Section 2). Lowering of the melting temperatures by network-modifying cations such as Ca, Na, K, Li, or Pb is well understood, as are the opposite polymerizing effects induced by the addition of Al. Raman spectroscopy (Chapter 2.2) is in particular used for rapid and nondestructive analyses of chemical bonds. The degree of polymerization of the coating is, for instance, derived from the ratio between the peak areas of SiO₄ bending and stretching modes (Figure 5), which markedly increases from fully depolymerized lead-rich glasses melted at about 700 °C to 3-D connected silica-rich glazes melted at about 1400 °C (Figure 5b and c) [14, 15, 18–22]. This direct relationship clearly illustrates how craftsmen have been unknowingly playing with the composition and degree of polymerization of their coatings to achieve the required properties.

Finally, the duration of the complete heating and cooling cycle is of course another important parameter, which is largely determined by the thermal resistance efficiency

Table 2 Modern glaze compositions expressed with Seger formula.

Glaze type	Cone	Acid	Amphoteric	Basic (flux)										
		SiO ₂	Al ₂ O ₃	ZrO ₂ (SnO ₂)	Fe ₂ O ₃	MgO	CaO	SrO	Li ₂ O	K ₂ O	Na ₂ O	ZnO	B ₂ O ₃	PbO (P ₂ O ₅)
Silica-rich	15	0.8333	0.0833				0.0583			0.025				
	7	0.7143	0.0816			0.0204	0.1429			0.0408				
Alkali-rich	11	0.6593	0.1209				0.1319			0.022	0.022	0.044		
	4	0.6275	0.0784				0.098			0.049	0.049		0.098	
Tableware	4	0.638	0.0673	0.0104			0.0878	0.0899		0.0251	0.0063		0.0752	
	4	0.6679	0.081			0.0223	0.0638	0.0911	0.0061	0.0152	0.0607		0.0506	
Majolica	1	0.6688	0.0495			0.0274		0.0547		0.0223	0.0983		0.079	
Low expansion	10	0.6477	0.0646	0.1062		0.0751	0.0262			0.0215	0.0138	0.0185	0.0277	
	1	0.5805	0.161	0 0.0113					0.1973	0.0295			0.0204	
Lead-based	4	0.6281	0.0753				0.0684			0.0165	0.0418	0.076	0.0606	0.076
	010	0.6599	0.0719											0.2682
	<022											0.1831	0.2958	0.5211
Aventurine	4	0.5795	0.0886		0.0453	0.0407	0.0724			0.0277	0.0954	0.0524		
Crackle	06	0.5461	0.0848				0.0039			0.0519	0.1426	0.0083	0.1617	
Raku	06	0.587	0.0723	0.0192		0.0023	0.0034			0.0362	0.1170	0.0056	0.1566	
Celadon	6	0.7422	0.0918		0.0029	0.0065	0.1206			0.0345	0.0011			(0.0005)
Chun/red	8	0.7718	0.0619		0.0064	0.0237	0.100			0.02604	0.0072			(0.0022)
Ash	4	0.316	0.0673		0.0062	0.0479	0.2561			0.030	0.1874		0.0827	(0.0053)
	8	0.4611	0.0996		0.0058	0.0269	0.1740			0.0346	0.1705			(0.0041)

Source: After [4].



of the insulating materials of the kilns. Many weeks were necessary for Chinese Dragon medieval kilns and a week was still common in the nineteenth century. Until the 1960s, complete firing cycles were then down to several days. Thanks to the replacement of bricks with oxide-fiber felts in the 1980s, they have now been reduced to a few hours or even a few minutes for floor tile production.

3.2 Metal Enamels

Bonding the glaze with the metal substrate involves a reaction with the oxidation layer formed at the metal surface. Copper and iron alloys have been first used because they develop easily on heating an adhesive oxide film. Coat and ground layers are added in modern enamels deposited on steel. Fluor addition promotes the reaction and the bonding (Table 3) [4].

3.3 Micro- and Nano-Structure

As determined by the starting materials and firing conditions, coatings display a wide variety of microstructures such as thin (Figure 6a) and thick (Figure 6b, e, and f) glaze layers or single (Figure 6a and c) and multi (Figure 6b, e, and f) glaze layers. When examined in section, Iznik fritware represents a good example of a complex multilayered glaze that results from many firing sequences. The thinner glassy coatings are obtained by the *salting* technique whereby NaCl, lead oxide, or plant ashes are poured (and volatilized) in the kiln, generally by the chimney when the kiln had reached its top temperature. The body can have a high (Figure 6a) or a low porosity (Figure 6b, e, and f), or no porosity at all (Figure 6c and d). Coarse quartz grains are obvious in Figure 6b, e, and f bodies (composite bodies exhibit a better mechanical strength). Examples of underglaze (Figure 6c) and overglaze (Figure 6d) painted décor are given. Note in Figure 6f, the very characteristic Iznik white quartz slip made of angular, crushed grains.

Because the glaze is almost liquid at the firing temperature, it is rather difficult to keep a sharp separation between adjacent colored areas. Different techniques have been used to limit this drawback, namely, direct

Figure 5 Structure and polymerization of silicate glasses. (a) Sketch of the network made of more-or-less connected SiO_4 tetrahedron with fluxing ions in between; (b) typical Raman spectrum showing the stretching and bending bands pertaining to the different types of tetrahedra (from Q^0 to fully connected Q^4), boson peak subtracted [16, 20–22]; (c) and (d) polymerization index (i.e. ratio of the bending and stretching band areas) for crystalline and amorphous silicates, respectively, after [20–22]; main fluxes and other oxides indicated.

Table 3 Representative metal enamel composition.

Enamel type	T_p (°C)	Acid		Amphoteric		Basic (flux)								
		SiO ₂	Al ₂ O ₃	ZrO ₂ (TiO ₂)	Fe ₂ O ₃	MgO	CaO	NiO (CoO)	Li ₂ O	K ₂ O	Na ₂ O	ZnO (BaO)	B ₂ O ₃	F (P ₂ O ₅)
Ground coat	805	0.4987	0.0382			0.0013	0.0718	0.0101 (0.0045)	0.0109	0.0103	0.1357	(0.0186)	0.1299	0.0650 (0.0016)
Cover coat	770	0.3905	0.0114	0.010 (0.141)		0.0019			0.0160	0.0438	0.0828		0.1205	0.1763 (0.0055)

Source: After [4].

painting on the green or porous body (underglaze décor), conservation of a line free of glaze precursor (often drawn with an oil-rich solution to avoid wetting by the glaze aqueous precursor, the *cuerda secca* technique), or addition of a highly refractory material such as either chromite [FeCr₂O₄] or spinel [(Mg,Fe)(Al,Cr)₂O₄] in Timuride and Iznik productions (Figure 3e) or hematite in Mamluk glass-enameled artifacts (Figure 3c and d). Furthermore, the hematite matt layer can be used as a rough substrate to attach physically a thin gold foil [18]. Another notable property of nonstoichiometric crystals such as spinels and chromites is their ability to catch diffusing ions.

Actually, many glazes contain micro or nanocrystalline secondary phases so that they are actually glass-ceramics (Chapter 7.11). Indeed, if the particle size is lower than ~1 μm, the optical clearness is kept. This is the case of calcium-rich glaze in which wollastonite [CaSiO₃] precipitates, common for Chinese and Vietnamese stonewares and *Celadons* [5, 9, 13], as well as for eighteenth-century soft-paste European porcelains. The growth of the crystalline second phase yields a specific décor largely experienced at the end of the nineteenth century and in contemporary creation (Figure 7d) [6]. Metal nanoparticles are another type of nanoprecipitates used as coloring agents as will be described in the next section (cf. Chapter 6.2).

4 Coloration

The color palettes on porcelain of the very beginning of nineteenth century of the Sèvres Manufacture (Figure 7a) are nice illustrations of the hues that were then obtained [11, 19]. Here, variations in hues were also determined by the different thicknesses of the enamel and small modifications of the composition [10, 11, 23]. As a general rule, the higher the firing temperature, the more difficult is the conservation of a large palette of shades. Because coloring agents were used in rather small quantities, elemental analyses either are not very efficient to identify them or involve very localized (destructive) methods [14, 24, 25]. Along with diffuse reflectance spectroscopy, Raman spectroscopy has proven to be the most efficient technique [2, 13, 15, 18–24, 26] especially when the frequency of the exciting laser is slightly higher than that of an electronic transition (the scattering intensities of bands coupled to this transition are then enhanced, and interferences with other bands reduced, which makes it possible to probe selectively chromophoric sites).

Glazes and enamel are colored in the same way as bulk glasses (Chapter 6.2). The simplest coloring agents are ions exhibiting electronic transitions in the visible range,

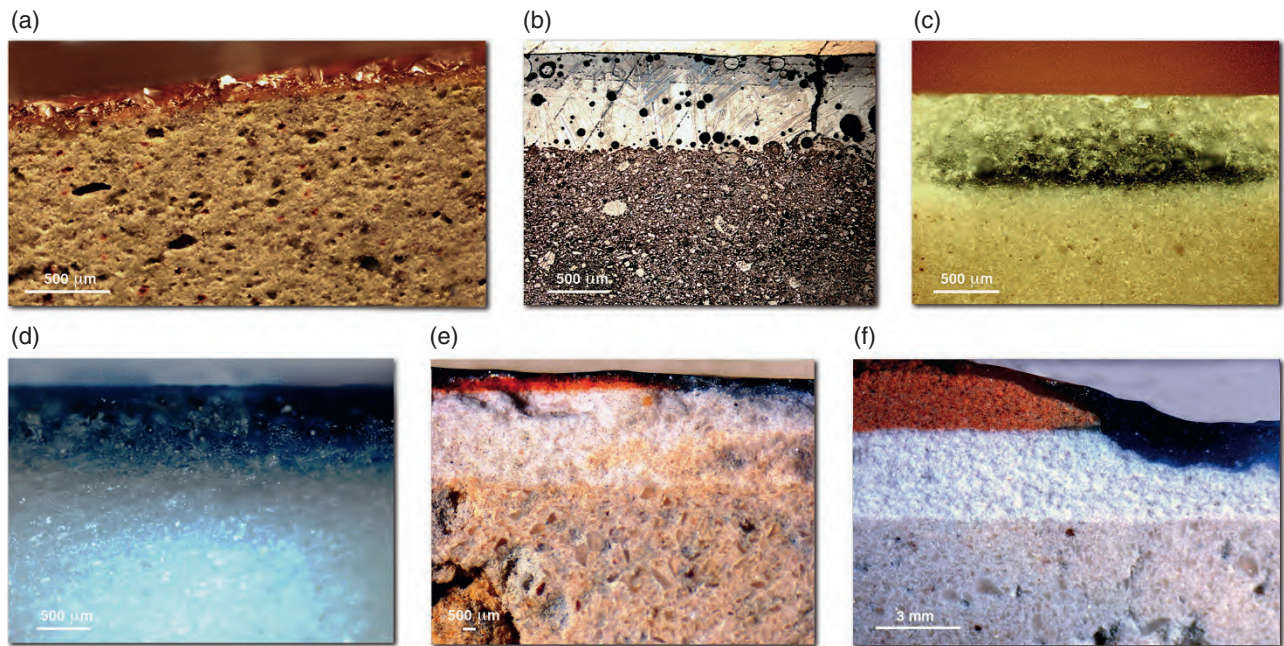


Figure 6 Optical/SEM micrographs of sliced sections of glazed potteries. (a) Lead-rich glaze on terra cotta (fourteenth century, Oman Sultanate, OM); (b) Ottoman lead-alkaline glaze on clay-rich tile tempered with quartz grains (fifteenth century, SEM); (c) Chinese glazed stoneware with an under-glaze dark blue décor (fifteenth century, OM); (d) Chinese blue over-glaze décor on porcelain (seventeenth century, OM); (e) Ottoman Iznik glazed tile, with a 3 mm-thick white quartz grain-rich slip over the body (fritware) and the multilayer glazed blue (top right) and red (top left) overglaze (sixteenth century, OM); (f) detail (OM). *Source:* Photos Ph. Colomban, except (e) and (f), courtesy G. Simsek.



Figure 7 Color palettes: (a) of painting enamel (~200 mm in diameter) for Sèvres soft-paste porcelain (nineteenth century, Sèvres Cité de la Céramique Coll.); (b) Ottoman Iznik polychrome dish decorated with red clove pink, ca. 1575–1580 (Sèvres Cité de la Céramique Coll.); (c) red flame glaze vase (end of nineteenth century, Sèvres Manufacture with crystallizations, Sèvres Cité de la Céramique Coll.) and details of a Plant ash glaze made by Brother D. de Montmollin (Private Coll.); (d) *fur hare* glaze (*Source:* Courtesy Jean Girel, potter, twentieth century, Private Coll.); largest diameter ~20 cm, except for details. *Source:* Photos Ph. Colomban (except (d), courtesy J. Girel).

such as transition metals (Fe^{2+} , Fe^{3+} , Co^{2+} , Cu^{2+} , Mn^{2+} , Mn^{3+} , V^{3+} , V^{4+} , etc.) or rare earths (Pr^{3+}), which are incorporated into the glass network. Depending on the ion, contents in the 0.1–1 wt % range generally suffice for efficient coloration. Because the electronic energy levels depend on the structural environment of the ion, the actual hue varies with the chemical composition of the glass matrix (Chapter 6.2). The effect is especially strong for Cu^{2+} , which yields turquoise and green colors in alkali- (Figure 2d) and lead-based (Figure 1d) silicate glasses, respectively. The variety of colors achievable in this way is limited, however. Other routes have thus been developed, especially for thin layers in which pigments can be incorporated without dissolving in the glass matrix if they are refractory enough [4, 6, 9–13, 19, 26–30] (Tables 4 and 5). Good examples are spinels, corundum [Al_2O_3], garnets [$\text{X}_3\text{Y}_2(\text{SiO}_4)_3$], and zircon [ZrSiO_4], whose very slow dissolution rates may actually cause real problems in glassmaking (Chapter 1.2).

A crystalline matrix can be specially prepared as a host for coloring ions to enhance color and tune it more precisely. The pigment then is synthesized independently and incorporated into the batch. The reactivity of the pigment should be sufficiently weak to avoid its dissolution/modification in the molten glaze, however, which is why highly refractory phases with compact structures such as spinels, corundum, garnets, and zircon are good matrices in this respect (Tables 4 and 5) [24].

Ancient pigments were usually silicate- and lead-based compounds. The same cuprorivaite structure [$\text{MCuSi}_4\text{O}_{10}$] has been used by Egyptian and Chinese craftsmen to prepare blue pigments, but with different alkaline earth cations, Ca and Ba, respectively. Natural pigments, such as lapis lazuli, a semiprecious lazurite feldspar colored through doping by S_x ions (Figure 3b and c), have been used at least since the Ptolemaic Dynasty to color pottery glaze and enamels on glass objects [18]. In the beginning of the seventeenth century, Johann Friedrich Böttger (1682–1719) took advantages of the high coloring power of lapis lazuli to whiten the glaze of the first porcelains made in Europe in Saxony at the Meissen Factory (Figure 2f) [31]. Alternatively, saturation in certain element leads to precipitation of phase(s) on cooling. Such a secondary phase precipitation can be tailored to opacify the glaze as done with cassiterite [SnO_2], fluorite [CaF_2], calcium antimonate [$\text{Ca}_2\text{Sb}_2\text{O}_7$], lead arsenate [$(\text{Pb,Ca})\text{AsO}_4$], and phosphates [2, 10, 11, 13, 24, 30–33]. Unmixing (Chapter 5.2) is another type of phase separation that is tailored for special effects, for example, for *aventurine*, *flamé* (Figure 7c), or *fur hare* (Figure 7d) glazes, sometimes in combination with the formation of copper or iron metal particles, respectively [34].

A third way is to use metal nanoparticles (formerly called colloids) as pigments or as light-diffracting agents.

Table 4 Pigments used in the twentieth to twenty-first centuries.

Pigments	Crystal structure	Color
$\text{Co}(\text{Al},\text{Sn})_2\text{O}_4$	Spinel	Blue
CoSiO_4	Olivine	Blue
$\text{CoAl}_x\text{Cr}_{2-x}\text{O}_4$	Spinel	Blue-green
$(\text{Zn,Fe})(\text{Fe,Cr})_2\text{O}_4$	Spinel	Black
CuCr_2O_4	Spinel	Black
$\text{Zn}(\text{Al,Cr})_2\text{O}_4$	Spinel	Pink
$3 \text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3 \text{SiO}_2$	Sphene	Victoria green
$\text{Pb}_2\text{Sb}_{2-x}(\text{Sn,Si,Fe...})_x\text{O}_7$	Pyrochlore	Naples yellow
$\text{ZrSiO}_4 : \text{V}$	Zircon	Blue
$\text{ZrSiO}_4 : \text{Pr}$	Zircon	Yellow
$\text{ZrSiO}_4 : \text{Fe}$	Zircon	Pink
$\text{ZrO}_2 : \text{V}$	Zircone baddeleyite	
$\text{SnO}_2 : \text{V}$	Cassiterite	Yellow
$\text{Al}_2\text{O}_3 : \text{Cr}$	Corundum	Ruby
$(\text{Al,Cr})_2\text{O}_3$	Corundum	Red
Cr_2O_3	Corundum	Green
$\text{Fe}_{2-x}(\text{Al,Ti,Mn})_x\text{O}_3$	Hematite (corundum)	Red
$\text{Fe}_{2-x}(\text{Al,Ti})_x\text{O}_3$	Hercynite (spinel)	Red
$(\text{Co,Ni})\text{O}$	Periclase	Gray
$(\text{Co,Zn})_2\text{SiO}_4$	Phenacite	Blue
$(\text{Ti,Ni,Nb,Cr,Sb})\text{O}_2$	Rutile-cassiterite	Brown
$(\text{Sn,V})\text{O}_2$	Rutile-cassiterite	Yellow
ZrSiO_4	Zircon	White
ZrO_2	Zircone	White
$\text{CdS}_{1-x}\text{Se}_x$	Wurtzite	Yellow (S) to red (Se)

Light is absorbed through its interaction with the electron gas formed at the metal/dielectric matrix interphase (Figures 1b, 2d, 7d and 8). The strong peak observed in the UV–visible absorption curve (Figure 8d) is due to the plasmon resonance of this electron gas and the broader features due to interband electronic transitions [27]. Typically, particles of gold, copper, silver, and iron yield ruby, red, yellow, and gray colors, respectively. Glaze colored with colloidal gold has been spuriously named Cassius purple [24, 27], after the chemist Andreas Cassius (1605–1673). The formation of metal nanoparticles requires controlling redox equilibria within the glass. Burning wet wood to produce hydrogen, which diffuses rapidly in the glass network, was a simple way to do it. Another, indirect way was fast diffusion of multivalent

Table 5 Main ancient pigments.

Pigments	Structure	Composition	Color	Date
Lazurite (Lapis lazuli)	Feldspathoid	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24} : \text{S}_x$	Ultramarine	Roman
Ultramarine	Zeolithe	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24} : \text{S}_x$	Ultramarine	> ~1830
Co-olivine	Olivine	Co_2SiO_4	Blue	>1500
Sèvres blue	Spinel	CoAl_2O_4	Blue	>18th
Egyptian blue	Amorphous	$\text{CaCuSi}_4\text{O}_{10}$	Blue	3000 BCE
Egyptian green		$\text{CaCuSi}_5\text{O}_{12}$	Green	3000 BCE
Han blue		$\text{BaCuSi}_4\text{O}_{10}$	Blue	500 BCE
Han violet		$\text{BaCuSi}_2\text{O}_{16}$	Violet	~200 BCE
Smalt	Amorphous	Co in glass		>1300
Bone white		$\text{Ca}_3(\text{PO}_4)_2$	White	Roman
Rutile	Rutile	TiO_2	White	>20th
Quartz	Quartz	SiO_2	White	>5th
Tin oxide	Cassiterite	SnO_2	White	>5th
Wollastonite		$\text{Ca}_3\text{Si}_3\text{O}_9$	White	>18th
Arsenate		$\text{Na}_{1-x-y}\text{K}_x\text{Ca}_y\text{Pb}_4(\text{AsO}_4)_3$	White	>16th
Uranyl yellow		UO^{2+} in (lead)glass	Yellow	>19th
Cadmium sulphide-selenide	Wurtzite	$\text{CdS}_{1-x}\text{Se}_x$	Yellow to red	>20th
Naples yellow type 1	Pyrochlore	$\text{PbSn}_{1-x}\text{M}_x\text{O}_4$	Yellow	Roman
Naples yellow type 2		$\text{PbSn}_{1-x}\text{Si}_x\text{O}_4$	Yellow	Roman
Naples yellow pyrochlore		$\text{PbSb}_{2-x}\text{M}_x\text{O}_7$	Yellow	Antiquity
Zinc yellow	Spinel	ZnCrO_4	Yellow	>19th
Mussif gold		SnS_2	Gilding	>13th
Hercynite	Spinel	$\text{Fe}_{2-x}(\text{Al,Ti,Mn})_x\text{O}_3$	Orange	Roman
Hematite	Corundum	$\text{Fe}_{2-x}(\text{Al,Ti,Mn})_x\text{O}_3$	Red	Roman
Pseudobrookite	Brookite	$\text{Fe}_{2-x}(\text{Al,Ti})_x\text{O}_5$	Red	Roman
Gold	Metal nanoparticle	Au	Red purple	15th
Copper	Metal nanoparticle	Cu	Red	<5th BCE
Silver	Metal nanoparticle	Ag	Yellow	12th

ions reduced at the glaze/enamel surface ($\text{Fe}^{3+/2+}$, $\text{Sn}^{4+/2+}$, $\text{Sb}^{5+/3+}$, and $\text{Eu}^{3+/+}$) [27, 28, 35]. Good examples demonstrating how aesthetic combinations of red and turquoise colors can be achieved through the different oxidation states of Cu ions obtained in kilns (Figure 7c) [32–36] are *Jun*, *flammé*, and Art Nouveau pottery.

A fourth method of coloration is based not on light absorption but on diffraction. The technique is extensively found in Nature (opals, mother of pearl, butterfly wings, beetles, cephalopods, or tridacna). The color arises from constructive/destructive interferences formed by the quasi-periodic organization at the layer nano-level. This surface effect is called *luster* (French *lustre*, from the Latin *lustrare*, to illuminate) (Figures 1b, 7d, and 8a). It dates back to the Islamic Abbasid dynasty (ninth

century) [27, 35–37] during which the alternation of layers rich and poor in metal particulates forming the luster was achieved by controlled sequences of oxidizing/reducing atmospheres by deposition of a mixture of Ag/Cu salt, clays, ocre, or organic compounds (vinegar, grape must, etc.) on the already glazed surface of the pottery. On heating ($\sim 600^\circ\text{C}$), silver and copper ions diffuse in the glaze and form metal nanoparticle-rich layers under the action of the reducing atmosphere and redox equilibria. Then the precursor mixture is eliminated by washing and the luster décor revealed [27, 35].

Gilding or *silvering* are yet other methods to coat a glass artifact with a colored metal layer of Au (Figures 1a, f, 2b, c, e, 3c [traces]) or of silver (Ag) [37]. Brass and mercury alloys are also used [39]. The metal layer can be bonded

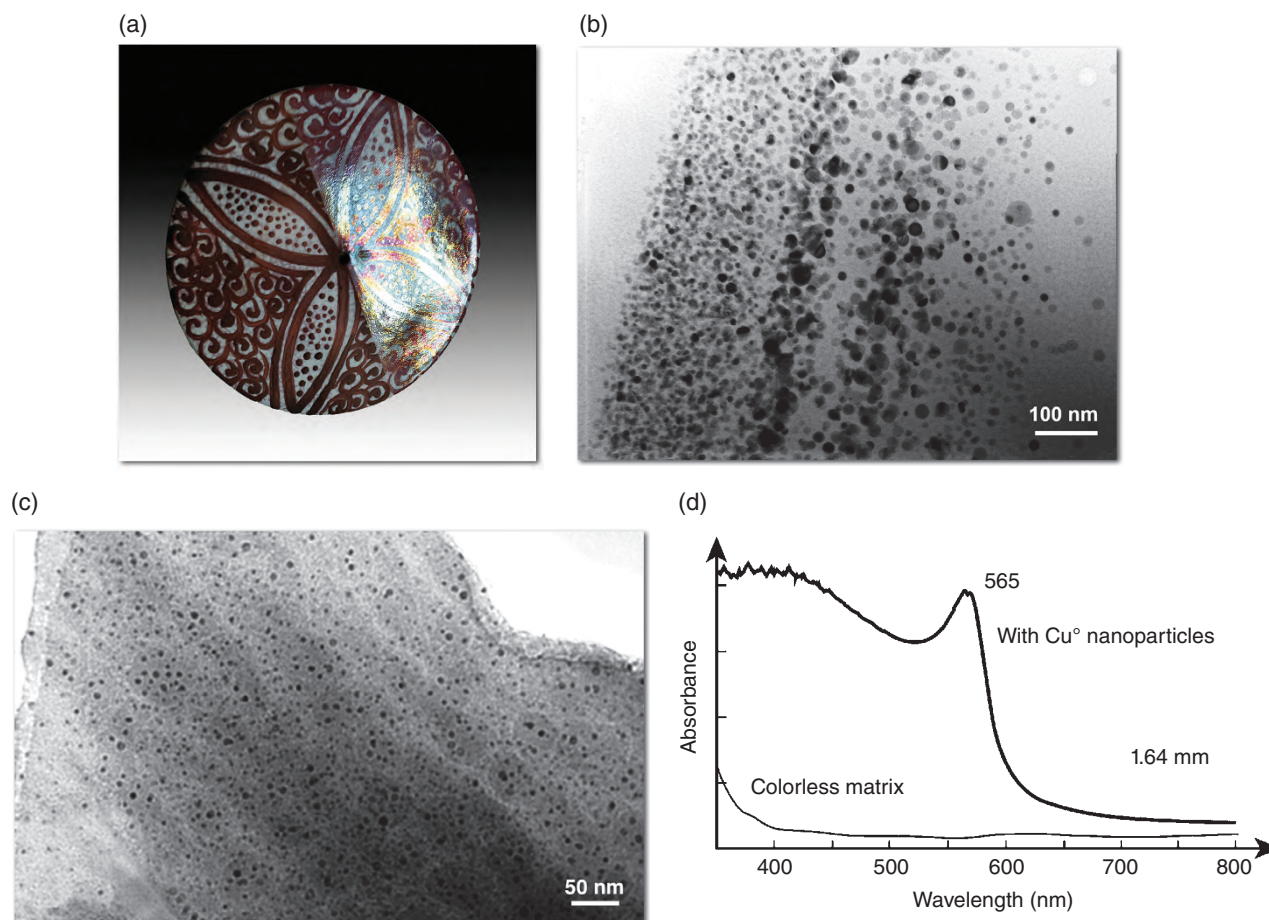


Figure 8 Glaze colored with metal nanoparticles. (a) Dish made by Eva Haudum, potter (note the golden and red shine for a given orientation; photo E. Haudum, diameter ~ 15 cm); (b) TEM images of a Fatimid luster pottery (twelfth century, Egypt) and (c) of a *pigeon blood* red glaze (Source: Courtesy Ph. Sciau, CEMES-CNRS, Toulouse); (d) comparison of the visible-light absorbances of a glass with and without 0.25 wt % Cu metal nanoparticles.

chemically or physically, thanks to a rough surface. Different techniques initiated during the Renaissance are possible (addition of Bi_2O_3 , resins, etc.). Finally, one obtains a white color by dispersing a second phase with a particle size comparable to that of the wavelength of visible light and a refractive index differing from that of the glass matrix. Examples are air bubbles, quartz, cassiterite (Figures 1f, and 6b), fluorine (Figure 1d), calcium phosphate, lead arsenate, zircon, or zirconia.

5 Enamels

5.1 On Metals

Early craftsmen first solved the fluidity problem by the *champlevé* technique (from the French *champ*, the background of the shield, in heraldry, and *levé*, removed), whereby the metal substrate was carved to form rifts that

retained the molten glass in the intended decorative pattern during the firing. More intricate decors were achieved in the second century BCE through the replacement of the carved regions with thin walls made up of metal foils called *cloisons* (thin walls, in French), a thin metal strip perpendicular to the substrate delineating the different colored areas and forms depicted (Figure 1d). The first were made by Celts on various metals and in Byzantium, mainly on gold. The *champlevé* and *cloisonné* productions on gold or silver substrates flourished throughout the Byzantine Empire and in neighboring Kiev and Georgia Kingdoms, as well as in the Western Carolingian Kingdom and Otton's Roman Empire (seventh to eleventh centuries) [2, 33]. In the twelfth and thirteenth centuries, Limoges (France) and Silos (Spain) became large production centers in relation to the Muslim culture of *al-Andalus*. Silver substrates were then used in Italy from the fourteenth century. Examples of compositions are given in Table 6.

Table 6 Mean compositions of some enamels on metal substrates.

Type	Origin	Date century	SiO ₂	CaO	K ₂ O	Na ₂ O	PbO
Painted	Limoges, Burgundy, Venice	15th	39–70	2.5–5	3–16	7–16	0–22.4
		16th	42–55	5–6.5	1–5.5	8–8.5	23–35
		16th	55–73	3	5–8	5–10	—
		16th–17th	62	4.5	4.5	—	2.5
		17th–18th	61	3.1	5.5	—	13.8
		19th	48	1.7	8	—	32.4
		16th–18th	53	6.4	5.2	—	27.2
Cloisonné	Paris and Spain	14th	60	2–8	4–15	9–15	0–2
	China	16th	40–45	5–6	8–10	0.5–15	30–37
		17th	45–60	5–15	5–10	0–5–10.5	15–22

Source: After [2].

A medieval Chinese report calls enameled work *production from the Devil countries* (*guiguo yao*), i.e. the West [33]. When the production of *cloisonné* enameled objects nonetheless eventually developed in China from the sixteenth century (Figure 1d), the technique had almost declined in Europe. The reason had been the emergence toward the end of the fifteenth century [2] at Limoges of a *painted enameling* (Figure 2a and b), an elaborate technique in use at the same time in Burgundy and the Netherlands as well as in other parts of France and Europe. Painted *Limoges* enamels consist of multilayer paintings deposited on a copper support through successive firings of different compositions (Figure 2a and b). The back side is also enameled and the *cloisonné* artifact polished after firing. This technique called *falang* (Frank, in Chinese) was more sophisticated than earlier ones such as *champlevé* with which the same glass matrix can be used for different colors. Like the potters of the *majolica* ceramics, craftsmen depicted very complex motives from episodes of antique legends or biblical themes. Around 1530–1540, yet another new kind of enamel employed a limited number of colors, mainly black and white (hence the name *grisaille*, grayness), to enhance the visual effects in the flesh areas of the human figures depicted. During the seventeenth century, the quality of enamels began to decrease until a remarkable revival took place in the nineteenth century: the workshops not only produced modern *Limoges School* pieces but also replicas of Renaissance enamels that were also often being sold as originals (Figure 2b) [2].

5.2 On Glass

Even though high-quality glass artifacts have been produced in large quantities ever since the beginning of Roman times (Chapters 10.3 and 10.4, [18, 23, 37]),

dichroic/luster and enameled glass (Figure 1a, and 2b, c) are very rarely reported in the ancient literature [10] or represented in museum collections [18, 23, 37]. Major examples of preserved enameled glass objects are remains of the Afghan Begram Treasure (first century CE; Musée Guimet, Paris), the fragments of the Lübsow cup found in Poland (second century CE), or the Cohn Beaker and Hans Cohn Collection, which is supposed to have been found in Egypt [18, 23]. The evidence becomes infrequent from these early periods until the Islamic and Venetian productions of the thirteenth century. The few remaining pieces representative of the whole Byzantine period are a group of gilded and occasionally enameled vessels from Corinth and Paphos together with a series of sparse objects, all dated between the tenth and the eleventh century, and the famous San Marco Bowl also dated to the tenth/eleventh century and probably brought back to Venice after the sack of Constantinople in 1204 by the Crusaders.

With the enameling and gilding technologies developed at the Norman/Swabian Court of Frederik II (recent excavation at Melfi Castle, Southern Italy, thirteenth century) and in Syria and Egypt [18] during the Ayyubid and Mamluk periods, pieces were then exported all over the ancient World from Europe to China. Mamluk Mosque lamps, mostly hanging, are among the most magnificent evidence of the technical virtuosity of those glassmakers. The use of lapis lazuli as ceramic or glass pigment has long been denied by scholars. But the presence of lapis lazuli powder, sometimes mixed with cobalt ore, has recently been demonstrated in pottery glazes and glass enamels of the fourteenth century [18]. Furthermore, a more ancient use of lapis lazuli has been documented down to the first century or even before with the glass treasure discovered in Afghanistan at Bēgrām or Ptolemaic glazed pottery from Pompeii [18].

The development of chemistry at the end of the nineteenth century offered a variety of routes to color a glass matrix and enamels. In France, Philippe-Joseph Brocard (1831–1896) and Emile Gallé (1846–1904) were very innovative craftsmen famous for their masterpieces (Figure 2c) [38]. Brocard's approach, the mixing of a variety of coloring agents, may have been related to his self-teaching of glassmaking, as opposed to the more traditional technology so that his expertise in various fine arts was representative of the nineteenth-century technical innovation spirit. On the other hand, Gallé took advantage of his traditional glassmaking expertise to create new forms, with innovative shapes and color associations, contributing to the novelty of Art Nouveau aesthetics. The most striking innovations at the turn of the nineteenth/twentieth century was the use of $\text{CdS}_{1-x-y}\text{Se}_x\text{Zn}_y$ semiconductor nanoprecipitates to prepare vivid red to yellow and of UO_2 ions for yellow glaze [4, 10, 26].

6 Glazes

As produced in the Middle East from about 2000 BCE, glazes were fired at about 900–1000 °C and colored or opacified with lead antimonate yellow [$\text{Pb}_2\text{Sb}_2\text{O}_7$] and calcium antimonate white [1, 24, 33]. More elaborate techniques were then designed, for instance, in Egypt by potters of the 22nd Egyptian Dynasty (945–715) who took advantage of an efflorescence phenomenon on the sample surface during the drying process to form an in situ layer of glass/coloring agent precursor [1]. Another notable feature was the real mass production achieved not only by Roman glassmakers (Chapter 10.3) but also potters with *sigillata* (stamped earth), for instance, exported in the first century as far as Syria, Egypt, and the Black sea from the Graufesenque workshops in Central France. The surface layer was intermediate between a glaze and a slip and colored with hematite [Fe_2O_3], hercynite spinel [FeAl_2O_4], or pseudo-brookite [$(\text{Fe}^{3+}, \text{Fe}^{2+})_2(\text{Ti}, \text{Fe}^{2+})\text{O}_5$] [25].

In the Far East, Chinese Eastern Han to Sui potters (second BCE to seventh century) really initiated high-temperature firing technology, thanks to the building of advanced kiln. Temperatures higher than 1300 °C were achieved as early as in the third century for the feldspathic Yue stoneware [5, 9]. The first glazes obtained using plant ashes were used as décor (Figure 1e) in a fashion that looks very modern from an aesthetic point of view.

White porcelains then appeared during the Sui and Tang Dynasties (seventh to eighth centuries) [5, 9]. At the same period, Islamic potters found how, when combined with low-temperature firing, the (fifth century) Roman glassmaking technique of opacification by cassiterite [SnO_2] could compete with high-temperature

fired porcelain to produce artifacts with complex depictions [5, 9, 34, 36]. This innovation resulted from the imitation of the three-color Tang Chinese porcelain wares with lead-rich blue and green glaze dots deposited on a faience/*terra cotta* body covered with an alkaline glaze [9]: the chemical reaction between the two glazes caused white cassiterite to precipitate. The use of cassiterite opacifier spread around the Mediterranean Sea with the expansion of the Islamic World, namely, in *Ifriqaya* (seventh century), *al Andalus* (eighth century), Sicily (ninth century), and then to Italy (*majolica*, thirteenth century) and France (fifteenth to sixteenth century) [29, 30, 35, 40, 41]. A composition shift took place from calcium-rich (ash-based) glazes during the tenth-century Five Dynasties to potassium-rich (feldspar-based) Song glazes (twelfth century) [5, 9]. Interestingly, a similar evolution took place with delay in Vietnam from the Ly to the Tran dynasties between the eleventh and fourteenth centuries [13]. Examples of compositions are given in Table 7.

Blue-and-white Yuan porcelains were first prepared with cobalt pigments that could come from Iran (or Saxony, Europe) through the Silk Road, thanks to the *Pax Mongolica*. Local cobalt ores were then used, but these Asian sources had high Mn and Fe contents. Especially when their fuel was coal, Chinese and Vietnamese potters empirically controlled the firing atmosphere of their kilns to obtain the strongly reducing conditions required to produce the blue color desired [9, 13]. As optimized in China, the blue décor was drawn on the body (underglaze décor, Figure 6c) or on the glaze (Figure 6d). The first technique was optimized in China while Vietnamese potters preferred overglaze décor.

Attempts to imitate the blue-and-white Chinese porcelain were first made by Islamic potters. Top-quality pieces were made in Anatolia, for instance, at Iznik (the ancient Nikaia) where manufacturer(s) developed fritwares between around 1450 and 1620 (Figures 6e, f, and 7b) [42]). In Italy, the Duke of Medici's porcelain (Figure 2e), a material intermediate between fritware and hard-paste China, was produced from about 1575 to 1587 with the help of a Master coming from the Levant [41]. At the end of the seventeenth century, manufacturers of soft-paste porcelain (silica-rich body made of a quartz grain cemented with a glass, a sort of fritware) appeared in France (Rouen, Saint-Cloud, Paris, Chantilly, Vincennes, Tournai, and Mennecey) before factories of hard-paste porcelain (Figure 2f) developed in the whole of Europe (Meissen, Strasbourg, Vienna, or Saint-Petersburg) [19, 40, 41]). Also called China, hard-paste porcelain is made from kaolin and feldspar. It is an alumina-rich body transformed into acicular mullite crystal frame (~30% in volume) soaked with a glassy matrix. The major difficulties were to build kilns reaching 1450 °C and to maintain such high temperatures for a few days. Consequently, the first European tentative at Dresden to fire

Table 7 Mean compositions of some glaze layers on terra cotta, stoneware, and hard- and soft-paste porcelain bodies.

Type	Origin/century	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	PbO	P ₂ O ₅	Fe ₂ O ₃	TiO ₂	MgO	B ₂ O ₃ (ZnO)
Terra cotta	Anatolia	27.1	3.8	2.1			62.8		3.02			
	Anatolia	40.4	10	1.8	1		42.9		2.9		1	
Celadon	Five Dynasty	59.4	16	16	3.4	0.3			1.8	0.4	2	
	Northern Song	63.2	16.8	13	3.3	0.6			1.4	0.2	1.1	
	Southern Song	68.6	14.3	10.4	5	0.1			0.7		0.4	
	Yuan	67.4	16.7	6.8	5.5	1.1			1.5	0.2	0.6	
	Yue 10th	58	12	20	1.5	0.8		1.5	2.2	0.8	2	
	Hop Lê	78.6	15.5	1.5	1.8				1.2	0.7		
	Koryo	73	17	0.5	2.6	0.8			2.5	0.9	0.5	
	Southern Song 10th–13th (Longquan)	67	14.5	10	5	0.5	—	0.6	0.5	0.1	1	
Hard-paste	Northern Song 12th (June)	71	10	10	3	0.5	—	0.5	<2	0.4	1.5	
	Northern Song 10th–13th (Ding)	72	17	3	2	0.5	—	0.2	0.5	0.2	2.3	
	Vietnam 15th	64	17	7	2.5	0.3	—		1.2	0.8	0.5	
	Yuan (b&w)	74.3	19.7		2.3	2.3		0.3	1			
	Böttger Meissen early 18th	61	33	4.8	0.1	0.2						
	Meissen 18th	59	35	0.3	4	0.8			0.3	0.1		
	Terre de Lorraine	64	30	1.2	2.3	2.2					0.2	
	20th	66.2	8.3	6.95	0.5	6.5			0.2	0.01	0.8	1.75 (2.2)
Soft-paste	St-Cloud	76	1.75	12.6	3.1	2.9	0.1		0.7	0.1	1.4	
	Vincennes	72.9	2.1	15.7	4.3	2.7	0.2		0.3	0.1	0.8	
	Sèvres	74.2	2.2	15.7	0.3	2.1	0.2		0.3	0.1	0.8	
	Terre de Lorraine	56.4	21.4	16.1	2.5	0.9		0.6	0.8	0.5	0.4	
	Bow (Bone ash)	45.6	8.7	23.6	1.1	0.8		18.6	0.6	0.5	0.6	
	Worcester (soapstone)	74.1	3.8	1.9	2.8	1	4.9			0.3	10.8	
	Longton Hall	77.2	2.9	8.8	3.7	0.8	6.3					
	Buon Retiro	79.8	4.65	0.2	2.1	0.5			0.4		12.4	

Source: After [5, 9, 11, 13].

hard-paste porcelain relied on a solar beam and lenses! Iznik potters first used a cassiterite opacifier in a lead-based glaze but rapidly replaced this technique by a layer made of crushed quartz grains covered by a transparent glaze (Figures 6e, f, and 7b). These grains act as light reflectors that give rise to the powerful colors of Iznik décors. The very efficient control of Ottoman authorities, the *Nakashame*, led to an exceptional quality of production for about a century [42]. Later, Kütahya manufacturers (Figure 1c) maintained the creativity of Ottoman glazed fritwares. Ottoman potters produced multilayer glazed artifacts requiring multi firing cycles (Figure 6e and f). The soft-paste porcelain route can actually be considered as an evolution of the Iznik fritware

technology since the body consists of quartz grains cemented with the frit. When kaolin was eventually discovered in Europe in the eighteenth century, its availability allowed for the preparation of hard-paste alumina-rich porcelain. Its high refractoriness led to design new glaze compositions. A revolution thus took place after 1750 with the development of fine faience and porcelain factories in Europe [19, 24].

Elegant white Song porcelains were largely exported, including in Japan. Throughout the thirteenth to sixteenth centuries, however, some Japanese scholars began to prefer Chinese and Vietnamese stonewares. Their simplicity and imperfections were more highly praised than the highly aesthetic Song style (tenth to thirteenth

centuries), as a result of the *wabi-sabi* Movement and the development of the Tea Ceremony [43]. During the Momoyama period (1573–1615), local potters, in particular those of the Raku Family, already very active, developed a highly original style (Figure 1f). Unpredictable kiln effects (i.e. defects!) were desired for these “accidentally lovely” works used as flower vases and utensils for the Tea Ceremony [43]. The discovery of this production at the first *Expositions Universelles* (World fairs) led to the *Japonism* and *Craft* aesthetic movements, which have largely inspired a large part of the contemporary pottery production. These have even been at the roots of the renewal of the *cloisonné* enamel technique in Europe at the end of the nineteenth century.

7 Perspectives

The second half of the twentieth century has seen extensive merging of companies in the ceramics and glass industries. Enamels formerly made in traditional manufacturing processes are now produced by a limited number of companies, which has led to a standardization of technologies and products. Only rare creative potters made again their enamels themselves. The best control of the heating (kiln) and insulation processes have also strongly modified the procedures whereas wood firing has almost disappeared. Some coloring elements have become either too expensive or toxic, in which case they are now prohibited (e.g. UO_2^{2+} yellow, CdS – CdSe red to yellow). As another example, the European Union plans to prohibit the use of lead, even if its encapsulation in silicate networks guarantees the absence of a reaction. Searches are being conducted to replace lead with other fluxes such as boron and bismuth although it remains to establish whether the new compounds obtained are actually less prone to release undesirable elements. On the other hand, sol–gel routes (Chapter 8.2) allow coatings to be processed at much lower temperature [44] than the usual ceramic and glass routes, which has led to innovative products such as enameled aluminum kitchen stoves.

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10.7

Venetian Glass

Marco Verità

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1 Introduction

That Venice has been the world leader in glassmaking from the middle of the fifteenth to the end of the seventeenth century is illustrated by Venetian artifacts exhibited in museums and collections all over the world. Venetian glassmakers always fostered innovation in terms of novel compositions, new glass designs, and applications so that their production was exported throughout Europe and the Levant. Even today the high-quality glass produced on the island of Murano is still living up to this long-standing tradition.

Several secrets were at the basis of this success:

- The style of Venetian luxury glassware and the skill of glass masters.
- The high quality of glass and the rich palette of colors, resulting from continuous improvements in the selection of raw materials and in the melting process.
- The variety of glass products such as luxury blown glass, but also tableware, lamps (*cesendelli*), chandeliers (since eighteenth century), window panes, mirrors, beads, glass for mosaics, enamels for metals and glass, imitation of gemstones, buttons, pigments for painting (smalt and *giallolino*), lenses for eyeglasses (Galileo Galilei selected Muranese mirror glass to make the lenses of his first telescope in 1609), glassware for alchemists, glass spheres for military use (to be filled with explosives), or even from the sixteenth century enameled glass for mosque lamps.

Throughout the centuries the development and success of the Venetian glass industry were strongly related to the support it was receiving from the

Venetian Republic which, in turn, exerted a tight control on it. As first documented in a 1271 text, glassmakers were, for instance, not allowed to leave the Republic and work in other countries to prevent trade secrets from diffusing out of Venice. Whereas the production of luxury glass was reserved to native Muranese glassmakers, luxury items could be sold only by the workshops where they were produced. As a matter of fact, these workshops had to alternate periods of production and of extinction of the furnaces in order to avoid overproduction. From the second half of the fifteenth century, product promotion was even provided since important personalities visiting Venice were brought to visit glass workshops in Murano (*Veder far veri a Muran*). Likewise, the Venetian government strictly protected the trade of the raw materials that were essential to obtain high-quality glass, ensuring regular supplies and forbidding their export to other glassmaking centers, but was forbidding the use in Murano furnaces of low-quality raw materials such as the potash plant ash in use in northern Europe.

The sources available today for a historical reconstruction of the Venetian glassmaking technology include archeological finds, analyses of glass remains, and historical documents. A significant number of archeological glass finds from the Venetian lagoon and towns near Venice (Ferrara, Padua, Verona, etc.) dating to the seventh to eighteenth centuries have been uncovered up to date. Archeological evidence of glassworking has also been found not only in the town of Venice but also in the island of Torcello, the most ancient settlement established along the Venetian lagoon after the end of the Roman Empire that quickly became a distant outpost of Byzantium with which close cultural and trade relations were maintained.

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Chemical analyses are available today for several hundred transparent Venetian glass samples, either clear or slightly colored [1–3]. These analyses concern glasses from museum collections and archeological finds, including waste glass and crucible fragments. Although the dating of most of the analyzed samples is generally reliable, it may be less so, for instance, when specimens found in an island of the lagoon were related to a building that had been in use for a long time.

Regarding historical documents, the fundamental reference for the study of Venetian glass is the chronology drawn up by Luigi Zecchin [4]. As stated by H. Tait [5], his researches “among the archives have done so much to correct long-established misconceptions and provide a sounder basis for the interpretation of the tangible remains from one thousand years of glassmaking in Venice.” Important contributions by other authors have also become available more recently.

Manuscripts drawn by the Venetian glassmakers themselves represent a unique source of information in this respect. These books date from the fifteenth century until today; they collected trade secrets written in the form of recipes describing how to select and process the raw materials, to prepare the batch, to color the glass, etc. As indicated below, some of them have been published.

- Three booklets (*Trattatelli*) attributed to the Tuscan glassmaking environment are kept in the State Archives of Florence, highlighting in some recipes the influence of Venetian technology. Their dating is still uncertain, ascribed to between late fourteenth and early fifteenth centuries by the first publisher [6] but to fifteenth (first half n. 1 and 2, second half n. 3) by L. Zecchin who extensively studied and commented them.
- The so-called Montpellier treatise, dated 1536 and also commented on by L. Zecchin [4].
- The *Anonimo* of the sixteenth century (reporting also recipes of the fifteenth century), the recipe book of a unknown Venetian glassmaker published in Italian and then translated into English [7].
- The treatise begun by Giovanni Darduin in 1644 who reported the secrets of his father Nicola (d. 1599) and then collected other recipes from different sources. After his death (1654), another author transcribed a number of recipes in an MS dated 1693–1712 [8].
- The recipe book of the Venetian glassmaker Brunoro found in Gdansk (Poland) written in 1645, including several North-European recipes demonstrating that the Venetian glassmakers working abroad experimented also with other techniques [9].

As for the famous *Arte Vetraria*, the first printed book devoted to glassmaking published in 1612 by the Florentine priest Antonio Neri (1576–1614), it also included a number of recipes of Venetian origin [10].

2 Raw Materials and Glassmaking

The oldest extant document related to the origins of Venetian glassworking is a manuscript dating from 982 CE, where a certain *Domenicus fiolarius* (Domenic the glassblower) is mentioned. Several documents of the eleventh to twelfth centuries then also mention the work of glassblowers.

The earliest documents reporting technical information are dated 1233 and 1255. They attest the import of raw glass and glass cullet from the Levant, suggesting that initially Venice was a center where glass made elsewhere was remelted and worked. The full glassmaking cycle is attested since 1255 (import of plant ash from the Levant) and 1275 (import of sand to make glass).

For fire safety, the glass industry was confined from November 1291 to the island of Murano where glass furnaces are still currently active. Only small furnaces for the production of imitation of gemstones were allowed to remain in Venice. From its origins to the end of the Venetian Republic (1797), the base material for the main production of Venetian glass objects was a soda-lime-silica glass. Historical sources describe the use of two basic raw materials.

Silica was used in the form of imported sand from the Levant, Crete, and Sicily or, from 1332, of better-quality pebbles from Ticino and Adige rivers (northern Italy) reduced to a finely ground silica powder suitable for melting. The use of pebbles instead of sand testifies to the efforts made in Venice to have a silica source less contaminated by coloring elements such as iron than the silica sands available.

As a flux, the Venetians used a soda ash obtained from burned coastal halophyte plants such as *Salsola soda* or *Salicornia* growing on high-salinity grounds. Already mentioned in ancient documents as *alume catino*, soda ash was imported from the Levant and Egypt (the latter of lower quality). From the sixteenth century, the import of soda ash from Spain (*barilla*) and southern France is also mentioned. Despite being considered of lower quality, this ash was increasingly used in the following centuries probably because of a diminution of the trade with the Levant. Unsuccessful attempts were also made during the eighteenth century to grow in the Venetian lagoon the plants to produce the flux.

In spite of its high freight charges, soda-plant ash was imported because it was a reliable raw material whose composition remained constant over a period of several centuries and allowed high-quality glass to be produced with the empirical technical knowledge available at that time. These ashes were complex mixtures of sodium and calcium carbonates along with of chlorides, sulphates, minor amounts of potassium, magnesium, iron, aluminum, silica and other elements, and coloring

contaminants at low levels. Lime is an essential stabilizing ingredient, the lack of which led to alkali leaching from the glass surface and weathering phenomena. This effect was first fully understood probably in Bohemia in the seventeenth century. During the Middle Ages and Renaissance, lime was thus unintentionally introduced in the right proportion with soda as a secondary component of plant ash.

A small amount of potassium (as 2–4 wt % K_2O) was also introduced through the soda ash (and feldspars present in the silica source). In some Venetian recipes, potash was deliberately added to the batch in the form of *grepolà* (tartar), the deposit of wine barrels, added in a calcined form (K-carbonate), or unprocessed (black tartar) as a reducing agent to obtain particular colors. Studying the Venetian recipes of the fifteenth to seventeenth centuries, P. Zecchin observed that the amount of tartar added to the glass batch increased progressively in this period [11]. Saltpeter (potassium nitrate) is rarely mentioned in recipes before the end of the seventeenth century.

The preparation of a lead silicate glass to be added to the batch, giving a soda-lime-lead-silica glass, is attested in Venetian treatises exclusively for the production of colored glass for the manufacture of rods, beads, imitation gemstones, enamels, and mosaic tesserae. The use of lead to improve the optical quality of colorless glass is found in Venetian treatises only from the end of the seventeenth century.

As first mentioned in a 1290 document, manganese dioxide was the decolorizer used by Venetian glassmakers to neutralize the color caused by the iron contaminants of the raw materials (Chapter 6.2). It was imported from Piedmont (Italy), Catalonia, Germany, and France. The Venetian glassmakers took great care in the decoloration process and brought it to perfection. Manganese was first added in small amounts to the batch. More of it was then added directly to the melt until decoloration was perceived. The addition of manganese was thus minimized, which manifestly improved the optical quality of glass. Arsenic and antimony associated to saltpeter were also used as decolorizers in Venice from the end of the seventeenth century.

Even though it was not mentioned in written documents, a very early trade of glass to Venice is attested by findings in the Adriatic sea, a few km off Venice, of a ship wreck with several hundred kilograms of raw, clear natron-type glass approximately dated eighth century [3]. In Venice, utmost care was taken in the selection of the cullet to be used for melting high-quality glass. Only in common clear glass elements indicating recycling have been detected analytically in trace amounts, namely lead and tin pointing to recycling of *lattimo* (a partially crystallized milky-like glass, Section 4.2.2) and copper to that of colored glass. Similar trace elements are found only rarely in high-quality *vitrum blanchum*, and *cristallo* (see Section 4.1).

Batch melting is attested in Venice from the thirteenth century, but was probably already practiced earlier. The process was performed in two steps, each workshop preparing its own batch. The first took place in a reverberatory furnace, the *calcar*, where the mixture of soda-plant ash and silica in nearly equal weights was calcined for several hours or days at about 800 °C to obtain the frit, an intermediate crystalline product. The batch had to be continuously stirred to avoid the formation of a vitreous liquid phase. The reactions taking place during this treatment led to the elimination of the carbonaceous compounds of the ash (avoiding undesired colors), the decomposition of carbonates (leading to release of gases and to better glass fining), and the transformation of the high-melting silica into alkali and alkaline earth silicates.

In the second step, the frit was melted in a crucible in a wood-fired furnace at about 1200 °C, possibly mixed with glass cullet and coloring and opacifying compounds. Analyses of crucible fragments of the eighth to thirteenth centuries found in Venice and Torcello have revealed the use of soapstone (magnesium silicate) whereas documents of the fourteenth to fifteenth centuries indicate that the crucibles were then made with clay imported also from Constantinople. During melting, one had to remove with a long-handled iron spoon the insoluble chlorides and sulphates present in the plant ash making up the scum floating on the surface of the glass, which otherwise would have affected glass transparency. A Venetian document dated 1348 mentions the technique of casting molten glass into water and remelting it subsequently. When repeated several times, this procedure helped to increase glass homogeneity by removing residual chlorides and sulphates salts, which were dispersed in the melt as small droplets and made the glass “obscure and cloudy.”

3 The Origins of Venetian Glass

3.1 The Transition from Natron to Soda-Plant Ash Glass

A number of scenarios have been debated for the origins of Venetian glassmaking. Besides more plausible hypotheses, some are clearly fantastic, to say the least, such as its introduction by Byzantine mosaicists of the eleventh to twelfth centuries, glassmakers from Altare embarked from Venice in 1096 for the First Crusade, or certain Benedictine monks.

The assumption of a direct connection with the Roman glassmaking tradition is based on the fact that Aquileia, a Roman town not far from Venice, was a famous glass-working center until the fifth century CE. Upon arrival of the Barbarians, Aquileia was destroyed and its inhabitants moved to the Venetian islands where they resumed

their activities, including glassmaking. Remains of glassworks were uncovered in 1960 during an archeological excavation close to Torcello’s cathedral. The initial hypothesis that they were related to the production of the mosaic tesserae for the basilica has been proved wrong by later analyses [12]. Instead, they attest to the presence of a glassworking activity on the island that has been dated to the seventh to eighth centuries, and was limited to the remelting of glass cullet and the blowing of items of naturally colored natron-type transparent glass (Chapter 10.3).

A second hypothesis associates the flourishing of Venetian glassmaking to the strong trading and political ties existing between Byzantium and the *Serenissima Repubblica*. In the tenth and eleventh centuries, Venetian

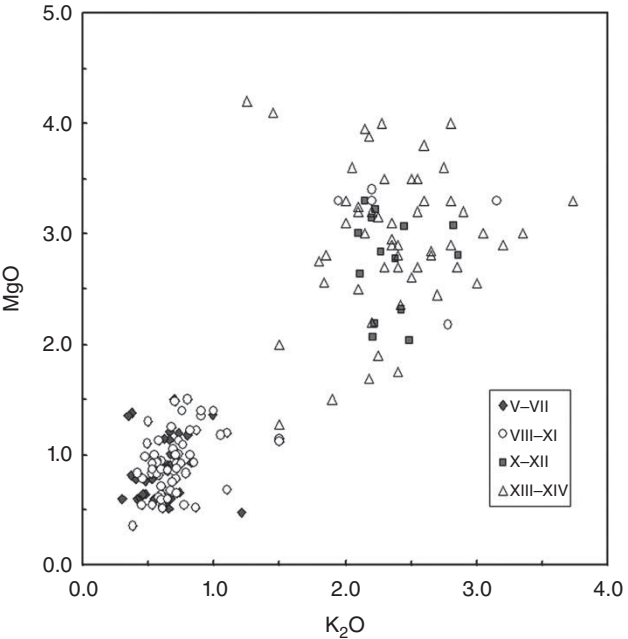


Figure 1 Changing origins of Venetian glass evidenced by variations in the analyzed MgO and K₂O contents from the fifth to the fourteenth centuries (time intervals indicated by Roman numerals).

merchants obtained the trading privileges from the Byzantine emperors that gave them a distinct advantage over their competitors from other western European cities. In that way, Venetians acquired Byzantine art and adapted and imitated its techniques, including the art of glassmaking that had not undergone the decadence brought about it in Europe by the fall of the Roman Empire.

As a matter of fact, valuable light on the origins of Venetian glass has been thrown by chemical analyses of clear samples dating from between the fifth and the fourteenth centuries. With respect to K₂O and MgO, the samples fall in two groups, which correlate with the relative ages of the glasses (Figure 1, Table 1). The earliest are characterized by the lowest fractions of K₂O and MgO, along with P₂O₅ contents lower than 0.2%, which point to the so-called natron glasses made by melting a silica-lime sand with natron as a flux. In some more recent samples of the eighth to twelfth centuries, non-negligible contents of tin, antimony, lead, and copper have been found. The presence of these coloring/opacifying elements at concentrations too small to affect transparency and color is considered as an indicator of remelting of glass cullet, which also contained polychrome opaque glass. The second group shows higher and more dispersed K₂O, MgO, and P₂O₅ contents. It represents glasses obtained by melting a batch of silica and soda-plant ash at a later period.

A few samples with intermediate concentrations of magnesium, potassium, and phosphorous (see Figure 1) probably indicate melting of mixtures of natron and plant-ash glasses. That in this period the two kinds of glass could be mixed to be remelted together is confirmed by the twelfth-century shipwreck found at Serç Limani (southern Turkish coast) whose cargo included three tons of raw glass and Islamic glass cullet of both natron and soda-ash types.

This transition from natron to soda-ash glass in the Venetian area is clearly pictured by the time histograms of Figure 2, where a marked change in the proportions of natron, natron-recycled, and soda-ash type glasses gradually took place between the eighth and thirteenth centuries. Until the seventh century, only natron glass

Table 1 Mean chemical composition and standard deviation of Venetian natron type (fifth–thirteenth centuries) and soda-plant ash-type (eighth–fourteenth centuries) glass samples (wt %).

Dating		SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	SO ₃	P ₂ O ₅	Cl	TiO ₂	Fe ₂ O ₃	MnO
Fifth to thirteenth centuries (natron)	Mean	67.1	2.18	17.7	0.67	0.96	7.36	0.26	0.12	0.97	0.13	0.81	0.68
	St. dev.	1.70	0.27	1.45	0.18	0.28	0.95	0.09	0.04	0.13	0.07	0.30	0.45
Eighth to fourteenth centuries (plant ash)	Mean	68.2	1.93	12.4	2.52	2.65	8.53	0.15	0.35	0.72	0.10	0.72	1.30
	St. dev.	1.43	0.45	2.05	0.41	0.50	1.15	0.07	0.08	0.15	0.03	0.35	0.48

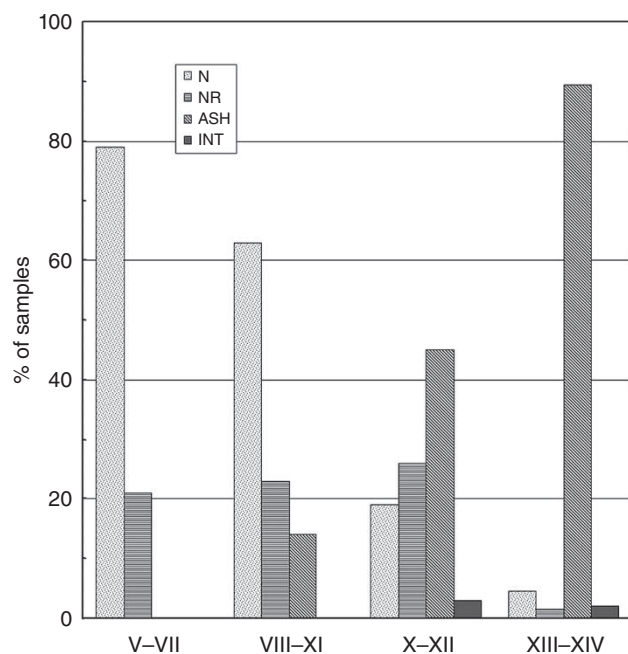


Figure 2 Transition from natron to soda-ash glass demonstrated by a histogram representing the fraction of analyzed samples belonging to each compositional group in the four time intervals considered: N, natron; NR, natron recycled; ASH, soda-plant ash; INT, intermediate composition between natron and plant ash type.

was used (1/5th recycled). Between the eighth and the eleventh centuries, the first plant-ash glass appeared at a time where almost 1/3rd of the natron glass was recycled. During the tenth to twelfth centuries, plant-ash glass represented almost half of the production, whereas natron glass was becoming mainly recycled. A few samples having an intermediate composition also date from this period. Finally, in the thirteenth to fourteenth centuries, almost all of the analyzed samples are of the plant-ash type.

A similar transition occurred in the Levantine world in the same period [13]. The presence of wood-ash glass has not been found, which further confirms a Levantine influence on the origins of Venetian glass. A group of objects and common glass scraps dating from the eleventh to fourteenth centuries could represent the earliest evidence for batch melting in Venice [14]. They are naturally colored transparent glasses with a level of contaminants (Al_2O_3 , TiO_2 , Fe_2O_3) higher than found in other samples of this period. The latter were probably produced by remelting of high-quality glass cullet imported from the Levant.

3.2 Torcello Mosaics

The technique of colored metal (silver or gold) leaves firmly adhering to hot glass slabs, which subsequently

protected them from oxidation and enhanced their brilliance, was first designed by the Romans (first centuries CE) and subsequently developed in Byzantium and Islam to make mosaic *tesserae*. Those of the eleventh to twelfth century Torcello mosaics give an interesting insight into the origins of Venetian glassmaking as they widely predate the earliest documents attesting in 1308 the manufacture of mosaic glass slabs in Venice, which permitted the production of 1500 *lingue* (i.e. tongues, gold- and silver-leaf elongated glass slabs) for the mosaics of St. Mark's cathedral in Venice, and in 1359 of other *lingue* for the Orvieto cathedral. An origin for the Torcello mosaics excluding a Venetian production has thus been suggested [15]. The raw glass would have been produced in Islam, then exported to Byzantium where it would have been remelted and colored. The *tesserae* (or glass slabs) would then have been manufactured and brought to Torcello by Byzantine mosaicists.

Against this explanation, which is not supported by factual evidence, one should note that chemical analyses distinguish between two groups of *tesserae*: whereas one was made with natron glass and opacified with calcium antimonate, the other (and more abundant) group was made instead with soda-plant ash glass and opacified with ground quartz. Now, the latter technique was peculiar to Byzantine *tesserae* as illustrated by other mosaics of this period made at Daphni and Hosios Loukas in Greece or at Monreale in Sicily. However, the glass of these *tesserae* is similar but not identical to that of Torcello, suggesting the use of similar but not identical raw materials to melt the glass [16]. Since glass *tesserae* subsequently made in Venice in the fourteenth century for St. Mark's mosaics are similar to those of Torcello, it seems justified to conclude that the Byzantine production technology of mosaic *tesserae* was transferred to the Venetian glassmakers at the time the Torcello mosaics was made, and then consolidated in Venice in the following centuries.

4 Venetian Renaissance Glass

4.1 The Secrets of Cristallo

Until the middle of the fifteenth century, Venetian glassmakers produced two qualities of clear glass (earliest documents, 1290), the so-called *vero comun* (common glass) and *vitrum blanchum* (white glass). We can suppose that *vero comun* had a slight green to yellow or blue natural hue, and that *vitrum blanchum* distinguished itself by the lack of any hue it had as a well-decolorized gray glass. As stated in Section 2, the glass quality was improved, thanks to four factors, namely the use of the less contaminated quartzite pebbles instead of natural sand as a silica source, direct addition of manganese into

the glass melt, careful selection of glass cullet, and casting of the molten glass into water.

Around the middle of the fifteenth century, a more dramatic change took place when a new glass called *cristallo* (crystal) was invented by the Muranese glassmaker Angelo Barovier (d. c. 1480). This name indicates a transparent glass with so much better optical properties (supposedly: perfect decoloration, less gray hues, and high light transmittance) than the traditional *vitrum blanchum* that it could be compared with natural rock crystal. *Cristallini* has been the term used since then to indicate items made with *cristallo* glass. Not only blown objects but also rods and beads were made with the new glass used also as a base material for transparent and opaque colored glasses.

The secret formula of *cristallo* was one of the main factors that allowed Venice to maintain its predominance over other European glassmaking sites for about two centuries. Venetian recipes dwell on the ways of obtaining *cristallo*. All of them agree that its “secret” lies in a preliminary step to be included into the usual procedure, which consisted in the purification of the soda-plant ash: the raw ash was dissolved in boiling water and the resulting solution was then decanted, filtered, concentrated, and dried to obtain a white salt called *sal de cristallo*. In general, one part of purified ash and one of powdered silica were mixed and calcined to prepare the *cristallo* frit, which was then melted for two days in a crucible. The glass was then poured in water several times and finally either decolorated by addition of manganese or colored with the appropriate elements.

The *cristallini* obtained in this way would have been practically sodium silicate glass because the purification process eliminated also the insoluble calcium and magnesium carbonates together with undesired iron compounds. It was thus unsuitable for making any kind of glass pieces since the lack of chemical stabilizers would have caused *cristallini* to bloom and crizzle even shortly after production. Of course, the well-preserved Venetian *cristallini* exhibited in museums and private collections demonstrate that Muranese glassmakers did search for a solution to this problem and found it.

The making of alkali silicate glasses almost free of lime and magnesia was nothing new. The existence of this kind of glass is attested by Florentine *basse taille* enamels of the fourteenth century, thus made well before the invention of the *cristallo*. A procedure similar to the aforementioned purification of plant ash was actually followed for preparing them. But stability against weathering was actually ensured by coloring agents such as copper and iron oxides, whose contents could reach 10 wt % to obtain the intense color sought after for the enamels to be thinly deposited on metals [17].

Analyses of fifteenth to seventeenth century Venetian clear glasses have allowed the secrets of the new *cristallo* glass to be deciphered. The analyses initially made [18] have now been confirmed by further work performed on more than 150 glass samples that were first classified visually. Samples with slight natural hues were termed “common glass” whereas colorless specimens were designated as either *vitrum blanchum* or *cristallo* depending on their more or less gray appearance, respectively. Iron and aluminum are contaminating elements of the raw materials considered as good indicators of their sources. Although there is some overlap between their contents in the three glass categories (Figure 3), distinct trends can nonetheless be identified as also shown by the compositional data gathered in Table 2.

The alumina and iron contents are the highest in common glass samples, indicating that these were made with the most contaminated silica sources. The 0.5–1 wt % alumina content of the *cristallo* samples is comparable to the values found for part of the *vitrum blanchum* samples (0.6–1.7 wt %). In contrast, the 0.2–0.4 wt % Fe_2O_3 content of the former is lower than the 0.3–0.8 wt % values found for most of the latter samples. Finally, it appears that the CaO (2.5–6.3 wt %) and MgO (0.5–2.4 wt %) contents in *cristallo* samples are significant; they are about half those of *vitrum blanchum* and common glass and show the same Ca/Mg ratio of about 3:1 as in the two other groups. The easiest way to obtain the *cristallo* composition was thus to melt a frit mixture of *cristallo* (free of alkaline earths) and *vitrum blanchum* in roughly equal amounts. This process yielded a glass of higher optical quality than *vitrum blanchum*, and ensured sufficiently high amounts of calcium and magnesium to stabilize the glass against weathering.

4.2 Other Renaissance Venetian Glasses

4.2.1 Enameled Glasses

The production of enameled glass is attested in Venice from 1280 until 1351 and then continuously since the middle of the fifteenth century. In the first period, the so-called Aldrevandin beakers were produced, whose name comes from the inscription below the rim of one specimen exhibited at the British Museum. In the nineteenth century, these beakers were attributed a Levantine source, in part because of a similar enameling technique used in Mamluk Islam to decorate precious vessels. The rediscovery of a number of records of painters of beakers operating in Venice between 1280 and 1351 and chemical analyses [19] have definitively ascribed them instead a Venetian origin. Although generally minor, the differences in composition between Aldrevandin and Islamic beakers are clearcut for the blue enamels that were

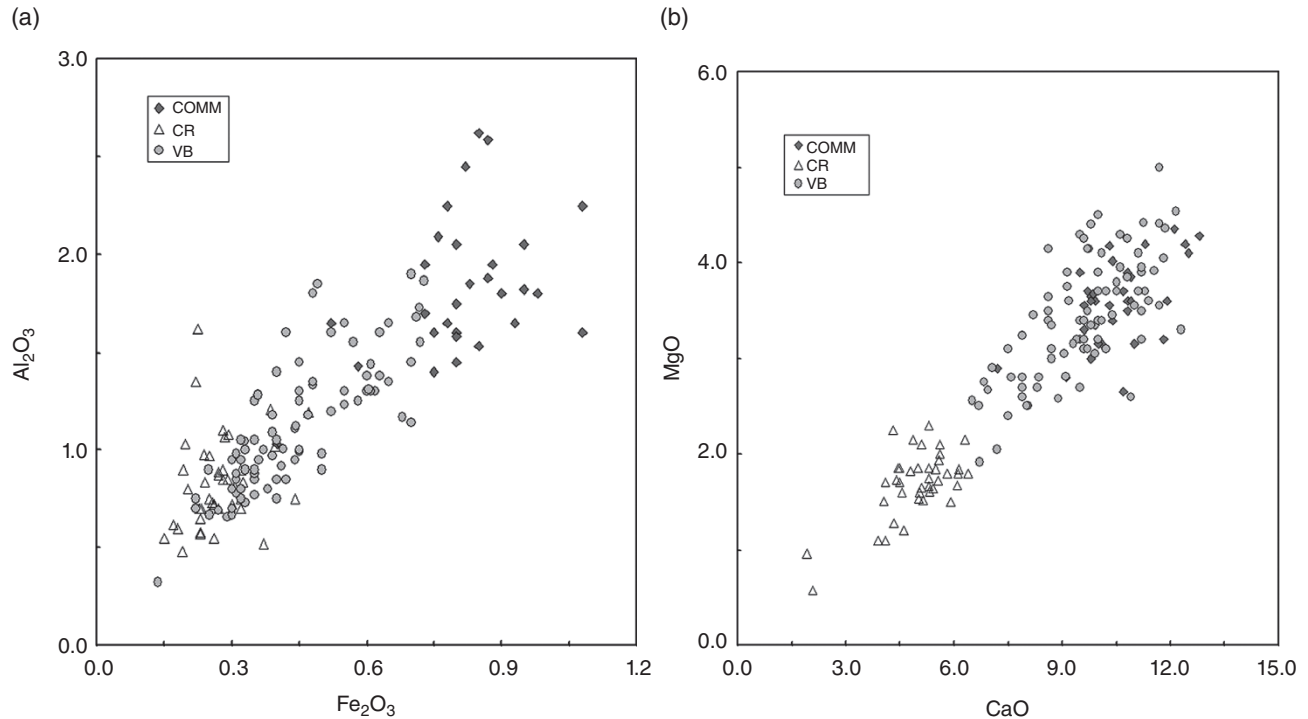


Figure 3 The mutual relationships between *cristallo* and *vitrum blanchum* established from plots of Al versus Fe contents (a) and Mg versus Ca contents (b). COMM, common glass; CR, cristallo; VB, vitrum blanchum.

Table 2 Mean chemical composition and standard deviation of the three groups of Renaissance clear Venetian glass (wt %).

		SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	P ₂ O ₅	Cl	TiO ₂	Fe ₂ O ₃	MnO
Common	Mean	65.2	1.82	12.7	3.04	3.58	10.5	0.31	0.72	0.08	0.79	1.02
(39) ^a	St. dev.	1.81	0.46	1.11	0.81	0.44	1.12	0.06	0.10	0.03	0.16	0.67
Cristallo	Mean	70.8	0.84	17.0	2.86	1.70	4.98	0.15	0.87	0.03	0.27	0.34
(45) ^a	St. dev.	1.23	0.25	1.24	0.41	0.35	0.95	0.04	0.17	0.01	0.07	0.13
Vitrum Blanchum	Mean	66.9	1.13	13.6	2.94	3.43	9.58	0.29	0.79	0.06	0.44	0.56
(91) ^a	St. dev.	2.02	0.33	1.45	1.08	0.62	1.42	0.06	0.12	0.04	0.14	0.30

^a In parenthesis the number of analyzed samples.

obtained with lapis lazuli powders by Islamic glassmakers and a cobalt blue glass by the Venetians.

Renaissance gilded and enameled glasses, mostly showpieces decorated with coats of arms, mythological scenes, etc., were made in Venice from the middle fifteenth through the seventeenth centuries (Figure 4) with a technique known from the description given in the second half of the fifteenth century by a manuscript kept at the University Library of San Salvatore in Bologna (MS 2861). Individual colors were obtained with glasses having different chemical compositions with different softening temperatures. After enamel powders had been deposited on it, the object was returned to the glassblower

for the firing process which was making the decoration permanent. The item was reheated, reattached to the pontil, exposed to the fire of the furnace until the enamels were fused, and then annealed. This process required great skill to prevent the object from being distorted and to avoid compromising the quality of the design by the difficulties raised by the differing viscosities of the molten enamels.

4.2.2 Lattimo

Lattimo (milk-like) was the Venetian term to designate the opaque white glass used until the middle of the fifteenth century only for the preparation of mosaics



Figure 4 Renaissance Venetian gilded-enameled ewer, c. 1530, height 20.9 cm, max diam. 12.7 cm (Museo del Vetro, Murano, Classe VI, n. 1004).

tesserae, enamels, and for small applications on blown glass. It was then improved by Angelo Barovier at Murano for producing luxury blown glassware to be gilded and enameled. This new glass was initially called *porcellano* (porcelain glass), because it was used to imitate oriental porcelain items that had just appeared in Venice. Objects

of *latesin* (light blue-gray opaque glass colored with copper or copper and cobalt) used for rare and precious objects are also mentioned in some documents dated 1496 and 1508.

Recipes to prepare *lattimo* report first the preparation of a lead-tin calx (lead and tin calcined together generally in a ratio of 1:1). Comparable amounts of *cristallo* frit and lead-tin calx and smaller amounts of silica were then mixed, calcined (frit), and melted. Manganese was added as a decolorizer. Analyses confirm that *lattimo* glass of fifteenth to sixteenth centuries was opacified by tin oxide crystals (cassiterite) dispersed in a soda-lime-lead-silica glass.

The term *lattimo* as applied to blown glassware appears for the last time in the Muranese documents in 1714. It continued to be used only for decorative threads and enamels. For blown objects, the new *smalto* (first in 1693) was then used. It was prepared by addition of arsenic oxide, saltpeter, and lead oxide to the traditional batch of *cristallo*. The *smalto* was opacified by micrometric crystals of lead arsenate, homogeneously dispersed, giving an intensely opacified glass with better properties (viscosity of the melt, smoothness of the surface of objects) and was less expensive than traditional tin-lead calx *lattimo*.

Other opacifiers such as calcium antimonate (from the mid-sixteenth century) and, less frequently, calcium phosphate (bone ash) are also mentioned in recipes. Darduin reports two recipes to make opaque white glass with antimony, which he describes as a rediscovered secret (*segreto ritrovato novamente*). It is not clear how the use of antimony reappeared in the glassmaking technology after a thousand years since it was a tradition in the Roman world. The chemical composition of Venetian white opaque glasses is reported in Table 3.

Filigrana (filigree) was invented in Murano in 1527 and further improved around 1540. This sophisticated decorative technique makes use of thin opaque glass threads twisted in different ways, encased in clear glass and incorporated into blown objects (Figure 5). The difficulties of working together *lattimo* and clear glass arose from the

Table 3 Chemical composition of opaque white Venetian glasses (wt %).

Dating		SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	Cl	TiO ₂	Fe ₂ O ₃	MnO	Sb ₂ O ₃	SnO ₂	As ₂ O ₃	PbO
Sixteenth century	<i>Lattimo</i> ^a	45.0	0.8	11.7	2.1	2.7	7.9	0.55	0.05	0.35	0.48		17.0		11.0
Sixteenth century	<i>Lattimo</i> ^b	49.0	1.0	16.5	2.2	0.8	2.3	0.65	0.03	0.25	0.05		15.0		12.0
Seventeenth century	Ca-antim. ^c	64.0	1.0	13.3	2.8	3.4	2.8	0.60	0.05	0.40	0.25	3.5			
Eighteenth century	<i>Smalto</i>	43.2	0.3	3.5	5.5	0.3	5.5	0.30	0.05	0.15	0.10			6.0	38.0

^a Lead-tin calx added to a *vitrum blanchum* base glass.

^b Lead-tin calx added to a *cristallo* base glass.

^c Antimony added to a *vitrum blanchum* base glass.



Figure 5 *Tazza*, filigree cup, c. 1550, height 9.0 cm, max diam. 17.9 cm (Museo del Vetro, Murano, Classe VI, n. 560).

different viscosities of the two glasses and the tendency of *lattimo* to form lump. They were overcome by Muranese glassmakers by a skillful technique involving rods made of a thin layer of *lattimo* between two layers of *cristallo* (Figure 6). The outer layer could be a colored glass, for instance, to prepare blue and white filigree.

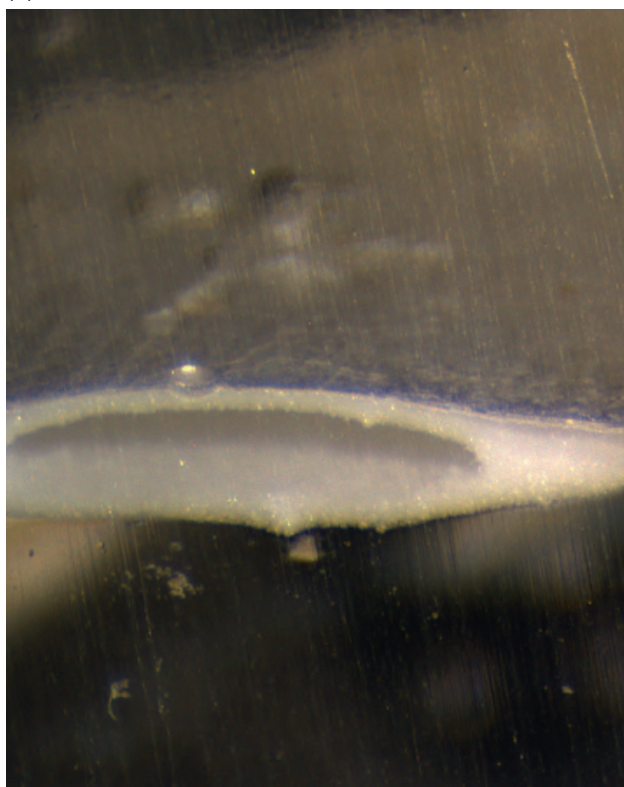
4.2.3 Colored Glass

“There is no kind of precious stone which cannot be imitated by the industry of the glass workers,” wrote the historian Marco Antonio Sabellico (c. 1436–1506) when dealing with Venice [20]. Colored glass was indeed one of the most distinctive aspects of the glassmaking in Venice where the manufacturing of colored glass rods, beads, and millefiori items is attested from 1338. Toward the end of the Republic in the late eighteenth century, these items even met with so much success that they became the major glass products made in Venice.

Colored glasses imitating natural gemstones (*verixeli*) are attested in Venice from 1281. The recipes deal with imitation of a variety of stones, e.g. blue (sapphire, lapislazuli, aquamarine, turquoise), yellow (amber, topaz), green (emerald, chrysophase), ruby red (ruby, cornelian, coral, garnet balas), purple (amethyste), and clear (rock crystal). Soda-lime-silica as well as soda-lime-lead-silica glass (with or without addition of potash) were used for this production that was exported to Europe and the Levant.

Angelo Barovier is to be recognized also as the inventor of chalcedony (Table 4), a layered glass with brown, red, purple, and yellow translucent or opaque layers (Figure 7) [21]. Venetian recipes for chalcedony call for a

(a)



(b)

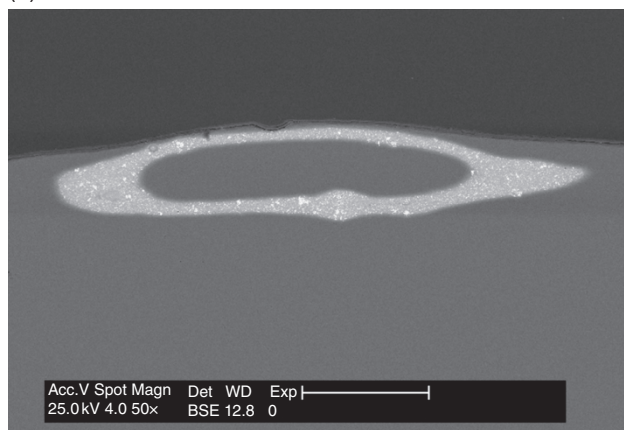


Figure 6 The thin *lattimo* glass rod embedded into a *cristallo* glass as seen in an oblique thin section examined by optical microscopy (a) and with scanning electron microscopy, back-scattered electrons (b).

lead-soda-lime-silica glass composition with coloring elements such as iron, cobalt, and copper; an amount of silver of about 1000 ppm was added directly to the molten glass immediately before shaping as nanoparticles coloring agent (Chapter 6.2). The chemical composition of a fragment of a sixteenth century Venetian chalcedony is reported in Table 4. Once the object had been fashioned,

Table 4 Chemical composition of colored Renaissance Venetian glasses (wt %).

Dating	Color	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	Cl	Fe ₂ O ₃	MnO	CuO	SnO ₂	As ₂ O ₃	PbO
Sixteenth century	Chalcedony ^a	67.0	1.0	14.0	4.8	2.0	6.2	0.6	0.7	0.2	0.5	0.5		2.2
Eighteenth century	<i>Girasole</i>	54.0	0.3	6.0	6.0	0.5	5.0	0.2	0.2	0.1			4.5	23.0
Seventeenth century	Aventurine	59.8	2.1	13.5	2.3	3.2	8.7	0.6	3.4	0.6	1.8	1.6		1.8

^a Content of 800 ppm of silver also measured.



Figure 7 Chalcedony cup decorated with droplets of aventurine, c. 1700, height 7.8 cm; max diam. 13.0 cm (Museo del Vetro, Murano, Classe VI, n. 1181).



Figure 8 Metallic copper particles dispersed in a nineteenth-century aventurine glass seen under the optical microscope.

the glassmaker was instructed to return to the furnace hole several more times to heat it until the chalcedony colors were seen.

Not to be confused with the homonymous green variety of quartz, *aventurine* (Table 4) is characterized by foliated, sparkling metallic copper particles dispersed in the clear (or blue colored) glass (Figures 7 and 8). It was mentioned for the first time at the beginning of the seventeenth century, but probably invented at the end of the sixteenth. Darduin [22] explained that the name *venturina* came from the fact that such a glass was extremely difficult to make and was obtained more by chance than by the skill of the glassmaker (*più per ventura che per scintilla*). Because copper was introduced as an oxide, the difficulty was first to reduce it with elements such as iron, lead, or tin (or even with cereal semolina) added to the melt at high temperatures and then to let the formed metallic Cu nucleate and grow crystals upon slow cooling down to the glass transition [22]. The chance character of the process thus resulted from that neither the overall chemical composition of the starting materials nor the thermal treatments were precisely controlled.

Given the importance played by temperature in both redox reactions (Chapter 5.6) and crystal nucleation and growth (Chapter 5.4), the temperatures obtained and their rates of change were often inappropriate to optimize reduction of copper oxide and especially formation of the Cu large crystals needed to ensure the quality of the final product.

The name *girasole* (sunflower) refers to a translucent, opalescent, dichroic glass changing its color from light blue (reflected light) to yellow reddish (transmitted light). The first reference to *girasole* glass appears in Neri's book, 1612 (Book 4, chapter 74), whereas the first mention in the Ricettario Darduin dates from 1 June 1693. The chemical analysis of a sample of the eighteenth century is reported in Table 4. The recipes for *girasole* and *smalto* are similar, prescribing addition to the *cristallo* batch of lower amounts of potassium nitrate, lead oxide, and arsenic oxide, which induced the separation of lead arsenate microcrystals [23].

Yellow pigments to color glass were called *anime* (souls) in Venice, with reference to the facility with which their color faded away during the shaping of the object.

The procedures to prepare *anime* in a range of colors from lemon yellow to orange brown are reported in Venetian recipes, which refer to lead stannate, lead antimonate, and lead-tin antimonate compounds [24]. The *anime* were added to a transparent, colorless (or green) molten glass and roughly stirred. The instability of the pigments once added to the soda-lime glass is emphasized by the recommendations to mix rapidly the *anime* with molten glass outside the crucible, on a metal plate.

5 *Façon de Venise* Glass and Competition

The rapid spread of Venetian glass was duly noticed by the clergyman William Harrison (1534–1593) [25] who wrote in his *Description of Elizabethan England*:

it is a world to see in these our days, wherein gold and silver most aboundeth, how that our gentility, as loathing those metals (because of the plenty) do now generally choose rather the Venice glasses, both for our wine and beer, than any of those metals or stone wherein before time we have been accustomed to drink.

From the sixteenth century onward, the increasing demand for Venetian fashionable luxury items encouraged a number of Muranese glassmakers (soon followed by Altarese glassmakers [see Section 6.2]) to set up glassworks all over Europe, where objects imitating Renaissance Venetian glass were produced in spite of the official bans. *Façon de Venise* productions are, for instance, recorded in Vienna (1486), Ljubljana (1526), Hall in Tyrol (1534), Antwerp (1537), Bohemia (1557), in the second half of the sixteenth century in London and later in Amsterdam (1597).

In most cases it is difficult to distinguish with the naked eye between genuine Venetian and *façon de Venise* glasses in view of their same styles and decoration techniques. Chemical analyses can be much more sensitive [26]. Three main compositions of *façon de Venise* glass have been identified: potash-lime-silica, mixed alkali lime-silica, and soda-lime-silica glass. The first two are typical of Northern Europe but were never made in Murano. The distinction between *façon de Venise* and genuine Venetian products is more complex for soda-lime-silica glass. Minor and trace elements characteristic of the silica source can help to distinguish them, however, Venetian glasses having, for instance, rather lower Zr concentrations in the 20–40 ppm range than *façon de Venise*.

Scientific investigations have been conducted within the framework of a project aimed at characterizing Renaissance Venetian enameled glass production and at providing analytical evidence to help distinguishing objectively these

items from contemporary *façon de Venise* or later imitations. In this case, analyses of enamels allowed further distinguishing criteria to be obtained [27]. For instance, particular chemical compositions are found, such as mixed-alkali base glass in *façon de Venise* blue enamels indicating the use of smalt (a potash-silica glass containing up to 8% of CoO used as a pigment). According to the written sources, Venetian glassmakers used an impure oxide named *zaffer*, and not smalt, as a cobalt source whereas the base glass of the blue enamels is of the soda-lime-silica type.

Besides the emigration of Venetian glassmakers, other reasons caused the decline of Venetian luxury glass toward the end of the seventeenth century. Neri's book (1612) unveiling secret Venetian recipes was translated in the following decades into English, Latin, German, French, and Spanish and probably inspired some of the experiments carried out by the inventors of new glasses in other European countries. In addition, glasses more brilliant and clear and less expensive than the Venetian *cristallo* were invented. This was the case of the potash-lime-silica crystal glass perfected by Johannes Kunckel (~1630–1703) in 1676 in Bohemia and of the lead (flint) crystal glass patented in England in 1674 by George Ravenscroft (1632–1683).

From the end of the seventeenth century onward, however, Muranese glassmakers attempted to renew their traditional *cristallo*. For instance, Giuseppe Briati invented a potash crystal glass similar to the Bohemian crystal glass. On the other hand, Venetian recipes of this period report the addition of significant amounts of lead to *cristallo* glass along with new decoloration processes with arsenic (or antimony) and saltpeter. But these attempts were not successful so that the Muranese luxury glass production decreased and nearly disappeared after the fall of the Venetian Republic. Venetian glassmakers did react to competition by specializing on other products. The manufacturing of small mirrors (in contrast to large mirrors made in France) to be exported in the Levant and glass beads destined in extremely high amounts for European colonies increased. Indeed, by the second half of the eighteenth century, the Venetian glass production had doubled in size compared to two centuries earlier [28].

6 Other Italian Glassmaking Traditions

Little is known of other glassmaking sites that were active in Italy (Milan, Ferrara, Mantua, Naples, and many others) during the Middle Ages and the Renaissance. It appears, however, that most of the glassworkers came from Tuscany, Altare, or Murano whereas written evidence attests to the production of utilitarian objects and more rarely of luxury glass.

6.1 Tuscan Glass

The importance of glass manufacturing in Tuscany between the thirteenth and eighteenth centuries is well documented [29]. As embodied by Benvenuto Cellini, a field of excellence of the Tuscan glassmaking was the manufacturing of enamels, which greatly influenced goldsmiths in Flanders and in France. The Florentine *Trattatelli* reported a number of recipes concerning enamels production. The base glass was made from silica (usually pebbles) and soda-plant ash. Addition of calcined tartar and potash plant ash was also reported. The fluxes were used as received or after purification. The technologies to make enamels in a wide range of colors and to opacify them are also described.

Archeological evidence of blown glass production in Tuscany dates back to the thirteenth century in the Valdelsa region. From the end of the fourteenth century and during the Renaissance, the glass workshops were generally established near large towns. Several documents describe the presence of Tuscan glassmakers in Murano during the fifteenth to sixteenth centuries, so that a production of luxury glass in Tuscany can be assumed.

Analyses of glass remains from workshops active during the fifteenth to sixteenth centuries indicate the making of soda-lime-silica glass. Some differences allow compositional groups to be identified [30]. A group characterized by low-alumina (Al_2O_3 1.5–2.5 wt %) and low-potash (K_2O 1.8–3.3 wt %) contents could have been made from silica pebbles and soda-plant ash imported from the Levant. A second group with high-alumina (Al_2O_3 3.5–5 wt %) and high-potash (K_2O 2.5–9.0 wt %) contents could have been made with a Tuscan silica sand rich in feldspars and the ashes of soda plants like barilla imported from Spain or southern France, but the voluntary addition of a potash source cannot be excluded.

6.2 Altare Glass

Altare in ancient Monferrato (today's Liguria), not far from Savona, has been a most important glassmaking center from the Middle Ages to the nineteenth century. The earliest document mentioning local glassmakers dates back to 1179. During the fifteenth century, more than 20 masters owned a glass furnace in this town. Whereas the guild kept a close control on glassmakers in Venice, regulations in Altare were much more liberal: the glassmakers could freely establish glassworks elsewhere so that they contributed much to the spread of glassmaking knowledge all over Europe [31].

Some Altarese glassmakers are related to significant innovations in the history of glass. Bernardo Perrotto (~1640–1709), for instance, obtained a French royal privilege to produce gold-ruby glass by using arsenic and gold

in his workshop in Orléans. This happened in 1668, that is 16 years before Johannes Kunckel began production of gold-ruby glass with another process relying on tin and gold on a rather large scale.

The Altarese Giovanni Odaccio Formica (fl. late seventeenth century) was working for Ravenscroft when he patented crystal glass in 1674 in England; he left Ravenscroft soon after and moved to Dublin (Ireland) to make lead crystal glass under another Royal patent. At that time, Ravenscroft opened a glasshouse at Hanley, where the master glassmaker was another Altarese, Giovanni Da Costa.

Whereas the activity of such Altarese glassmakers working in Europe is well documented, very little is known of their glassmaking technology for neither archeological evidence nor analytical data for genuine Altare glass items are available at present.

7 Perspectives

A sufficiently comprehensive picture of Venetian glassmaking from its origins to the Renaissance is emerging as a result of documentary research, archeological research, and chemical analyses. Some aspects concerning the provenance, dating, and selection of the samples limit the information obtained. Further analyses of well-dated samples of certain provenance are required for this purpose.

The compositional distinction between the Venetian and Levantine and *façon de Venise* glass production will require analyses with high-sensitivity techniques and determinations of the isotopic compositions of the samples.

Although the seventeenth and eighteenth centuries are generally considered as a period of decline for Venetian glassmaking, they were characterized by a great renewal in competition with other glassmaking centers in Europe. The considerable amount of written evidence available for this period has not been thoroughly examined so far, and relevant analytical data are almost completely lacking. The same can be said for the nineteenth century – the century of the Muranese glass rebirth – and for the twentieth century.

Only few analyses of colored Venetian glass have been published until now, and a comprehensive picture of this peculiar Muranese production is far from being accomplished.

Enormous amount of glass were made at certain periods to make beads, which became the predominant production in the eighteenth century. The required palette of colors was extremely broad in spite of the requirement that the thermal expansion and viscosity of the different glasses used to make polychrome beads had to be

matched. As very few analyses exist, specific research on available documents and materials deserves further study. Equally insufficient are the analyses made on imitation gemstones.

Little is known so far of other Italian glassmaking centers. The major innovative role played by Tuscan glassmakers in the medieval production of enamels is still underestimated because of the scant information available. Altarists introduced major innovations in glassmaking and contributed to develop the glass industry north of the Alps. Unfortunately, the Altarists' glassmaking tradition is still nearly unknown.

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10.8

Stained Glass Windows

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1 Introduction

Throughout the time of the Roman and Byzantium Empires, and later in much of Europe, glass competed with less expensive materials such as waxed linen, shell, horn, sheets of mica, or thin layers of alabaster as a means of glazing. In the brilliant sunshine of the Mediterranean region, limiting the light transmission and reducing solar heat gain in summer were significant factors in window design. As the Romans extended their domain northward, however, the importance of achieving adequate internal light levels increased and the greater transparency of glass was at a premium. Over the same period, the introduction of colored glass sheets offered new decorative possibilities. Consequently, for those who could afford it, glass became the material of choice. The resultant demand stimulated its production, motivated process improvements (Chapter 10.9), and simultaneously inspired architectural developments [1].

Glass windows were used by the Romans in domestic settings and civic buildings, but the availability of sufficiently large sheets led the expanding Christian community to use them in churches not solely for lighting and decoration but also for spiritual reasons. Genesis, the first book in the Bible, spoke of God's first creative act as a division of light and darkness. Phrases like "Then God said, *Let there be light; and there was light*" underpinned ecclesiastical thinking. Light and windows were inextricably linked. The stream of light into the main body of a relatively dark church would have shouted out to visitors, adding dramatically to a sense of worship; this feature

was widely appreciated in these early buildings even from Roman times as shown by comments in the literature of the period.

As early as the fourth century, the colored glazing of the basilicas in Constantinople was considered worthy of mention by the Roman poet Prudentius (348–aft. 415) in his praise of the good emperor who "covered the curves of the arches with splendid glass of different hues, like meadows that are bright with flowers in the spring" [2]. An advantage of colored glass recognized early on was the facility to display images in sizes much larger than those of individual glass panes. In addition to their spiritual and decorative effects, images of biblical and other religious themes represented valuable teaching tools at times when most people were illiterate and when, in the West, the Latin language of the liturgy was generally not understood. Colored glass was expensive, however, so that its use remained more common in religious than in civil architecture; only the wealthiest could afford it for their manors and princely houses. Until the nineteenth century, the development of stained glass has, therefore, been intimately connected with the evolution of its religious setting.

The limitations of cost as well as of technology restricted early glazing to simpler designs with a limited color palette and this still remains the case in the less critical areas of churches. Nevertheless, at least from the Byzantine period colored glasses have been organized into simple pictures representing aspects of the church's story. The fact that the only glass available was imperfectly flat meant that it would slightly distort the images of objects outside the building, making the window itself the center of attention and diffusing light sufficiently to avoid obvious transmitted images on the floors and walls. The introduction of silver staining in the 1300s added to the complexity of images that could be produced. It was

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another revolutionary step in developing decorative glazing, which was acknowledged by the English language in the nineteenth century when such glazing was termed *stained* rather than *decorated* glass.

Because the development of stained glass first and foremost relied on the availability of flat glass with fire-polished surfaces, this chapter begins with the crown and cylinder processes, the latter being still used. Attention will then be paid to the social contexts that were at the roots of the extensive use of stained glass in the West. Next, the ways in which glass was colored in the bulk, decorated on its surface, and integrated into a frame of lead strips are reviewed. Finally, the evolution of stained glass from the nineteenth century and the problems raised by the conservation of old, corroded windows are described. Given its limited size, this chapter is of course not comprehensive so that we refer to some of the many excellent papers and books available for more detailed accounts [e.g. 3–6]. Further information is also available from national and international organizations publishing research in the field. An example of such publications is the *Corpus Vitrearum Medii Aevi*, created at the initiative of the Swiss art historian Hans R. Hahnloser (1899–1974) in the form of an extensive series of illustrated catalogs of stained glass windows published by national committees under the auspices of the *Union Académique Internationale*.

2 Making Glass Sheets

2.1 Cast Window Glass

The oldest documented mansions and public buildings glazed with glass were built in the Roman Empire where transparent material was already produced on a large scale in the Levant in melting tanks whose capacity could reach 20 tons (Chapter 10.3). Initially, panes were made from glass cast in the molten state into a rectangular arrangement of iron bars forming a tray on a stone base perhaps covered by clay. Alternatively, the base might have been made of wet wood. Such large cast sheets have, for instance, been found in the glazing of Pompeii. A second-century bath-house window made by this technique in a Romano-British iron-working settlement at Hartfield, East Sussex, in the United Kingdom measured 235 by 255 mm and is now in the British Museum.

Inevitably, such glass slabs had a seriously disfigured surface where the glass contacted the solid casting substrate. In addition, rapid chilling of the molten glass followed by cooling of the thick slab gave rise to ripples on its lower surface while any sand, grit, or asperity on the casting substrate resulted in pock marks (Figure 1). It therefore fell into disuse until the end of the Middle



Figure 1 Cast Roman window glass: ~4–5 mm-thick, originally 35 × 80 cm panes, generally greenish, thinner at the edges with a fire finish on one side and a rough surface and tool marks on the other, found in a mid-third-century CE shipwreck off Ajaccio (Corsica) [7]. Source: Photo Hervé Alfonsi, ARASM; épave *Porticcio A*.

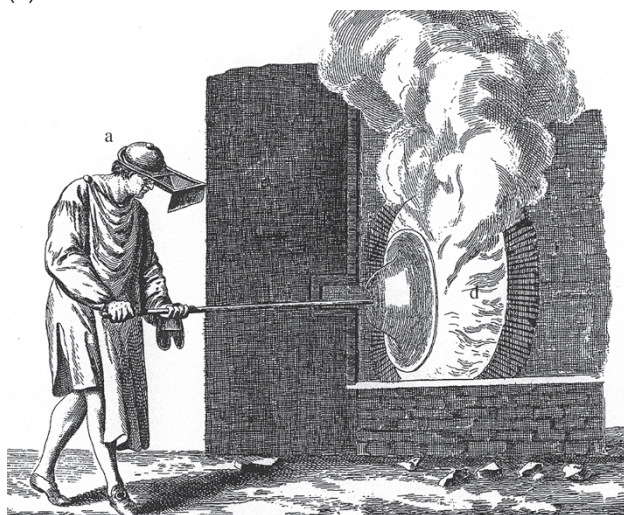
Ages when slow process improvements led to higher quality surfaces. These included the use of copper- and then iron-lined tables, the ability to suspend and control bigger crucibles over them so that larger sheets could be poured, the rolling of the hot glass, and the introduction of mechanical grinding and polishing in the early twentieth century (Chapter 10.9).

2.2 Crown and Cylinder Processes

In early Roman times, the introduction of blowing irons for shaping glass had also given a major stimulus to glass production, particularly of containers (Chapters 10.3 and 10.5). Because the new process allowed pristine glass surfaces to be produced with a fire finish, the idea came that, to have the same finish, flat glass had to be made from blown hollow ware. Two different processes were invented for this purpose. One was the *crown* method (Figure 2a). It involved first blowing a flattened bubble in the shape of a hollow disc, then attaching a *pontil* rod on the reverse side for support while opening the disc up where the blowing iron had been attached. Finally, the hollow disc was reheated and spun rapidly so that the centrifugal forces caused it to flip dramatically into a circular sheet of glass. The panes, which were significantly thinner than when produced by casting, were cut from the outer rim whereas the center where the pontil rod had been attached was of poorer quality and of less interest to the glazier. Of course, the imaginative window designer was sometimes able to incorporate such pieces with their *bull's eye* into his work.

The earliest samples of whole discs date back to the fourth century. They were small, measuring no more than 200 mm across. Because of the way it was made, this type of glass was slightly convex and had circular features, for instance, in the trails of bubbles trapped in the glass.

(a)



(b)

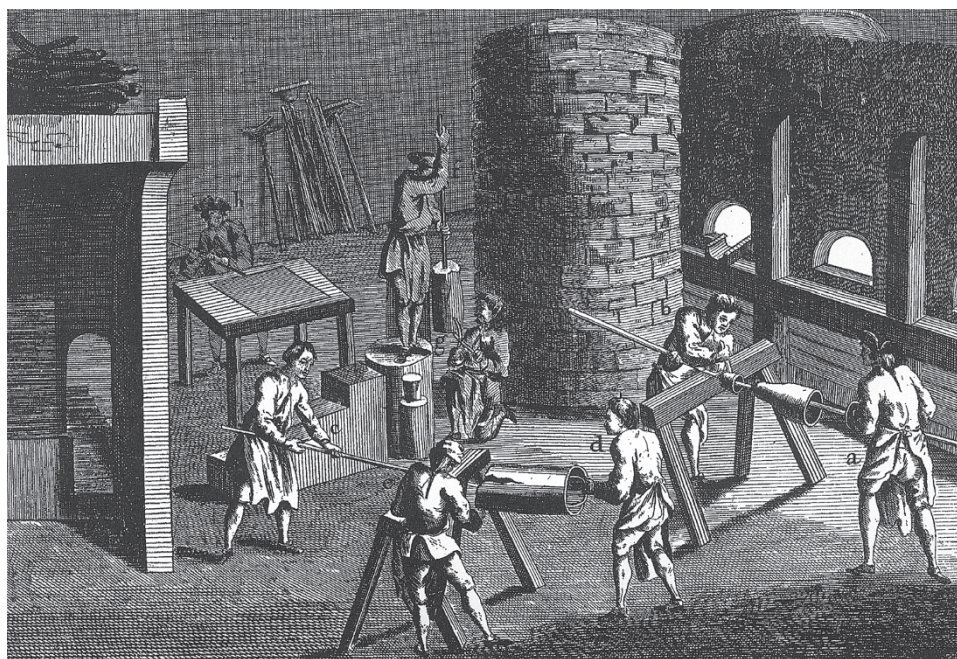


Figure 2 Final steps of the making of flat from hollow glass before annealing in dedicated furnaces as depicted in the *Encyclopédie* of Diderot and D'Alembert [8]. (a) Crown process: flattening by rapid spinning under the heat of the furnace of a vessel that was first blown, attached to a pontil at its other end, and opened wide on the blowing side; (b) cylinder process: cutting of the ends of a blown cylinder [a, b], longitudinal splitting with scissors [c], opening of cylinder [d], and flattening [h].

These make its origins identifiable even from relatively small fragments. Sections cut from a larger disc have been found in excavations near the church of San Vitale in Ravenna, Italy, dedicated in 547 CE, one fragment having evidence of rudimentary Christian symbols drawn on it [4]. The process continued to be developed over time. During the twelfth century, it became known as the Normandy method after its main area of production. Much larger discs could be made, thanks to further technical

improvements and to the greater quantities of glass that could be melted in a single pot. By the fourteenth century, these were up to 600 mm across. In 1700, the best discs were Dutch and reached 800 mm; Norman glassmakers responded to this challenge since their sales ledgers from 1724 reported that diameters of just over a meter (in modern units) were available [4].

The other method for making flat glass was that of the *cylinder* (Figure 2b). It also had its roots in Roman



Figure 3 The palette of hues described by Theophilus exemplified at the same period by the portrait of Hosea, one of the four prophets pictured in the 1130s in Augsburg cathedral. Glass probably made in the Benedictine abbey of Tegernsee, 100 km South-East of Augsburg. Modern framing of the stained glass with alabaster, a translucent material that could also be used for windows. Source: Photo P. Richet.

technology since it appeared toward the turn of the third and fourth centuries (Chapter 10.5). As part of a detailed picture of house glazing, its earliest description extant is that of the twelfth century by the German monk and priest Theophilus [9] according to whom a large palette of hues was commonly available, including *album* (white), *purpureum* (purple), *membranaceum* (flesh colored), *saphireum* (blue), *rubicundum* (red), *viridium* (green), *croceum* (gold yellow), or *luteal* (saffron yellow) (Figure 3). By swinging a blown bulb vertically, the worker stretched it in the form of an elongated cylinder and controlled its diameter by *marvering* it (i.e. rolling a glass gather on a marble table) and by manipulating it with

various tools. This *long bladder*, as termed by Theophilus, was finally cut longitudinally – hot with scissors or cold with a red-hot iron – opened and flattened with a type of wooden rake in a softening *lehr* to make a flat sheet. The product was variously known as *cylinder*, *broad*, *sheet*, *spread*, or *muff* glass. Sheets made in this way can be identified by the elongation of internal bubbles along the axis of the cylinder.

From the fourteenth century, Lorraine became a significant European center in the production of cylinder glass, thanks to abundant wood and high-quality sand resources and to immigrant labor from Bohemia where no doubt the early Roman traditions had been maintained and developed. Often termed *Lorraine glass*, this material was linked to a major improvement in quality, for example, less variability in thickness, and cylinders were up to 1.5 m long. By this time, improved controls of temperature and other operating parameters meant that both surfaces of cylinder glass were glossy, unlike those of early Roman production.

These manufacturing methods were steadily improved over the next centuries but not radically changed until the introduction of mechanized processes at the beginning of the 1900s (Chapters 1.4 and 10.9). At least early on, the crown method gave a higher quality surface finish – “brighter and more transparent” – because it was fire polished on both sides. It was more expensive, however, and involved a higher proportion of waste in its production and cutting as it could not yield panes larger than 16 × 12 in. out of crowns 30–32 in. in diameter [10]. Cylinder glass had the major share of production and differing requirements led to differentiation between Franco-German, Bohemian, and German, and Belgian, English, and American types [10]. In part, this diversification resulted from the desire to make “whiter” and bigger glass panes for larger windows. This required a change of composition toward those of *short* glasses (Chapter 10.5), which could be blown into cylinders that were not as long but had a larger diameter [11].

The final choice of crown, cylinder, or cast glass depended partly on application and partly on fashion, which could vary between different countries. Cylinder glass gave larger sheets but crown glass was of better optical quality. Costs were another factor, including taxation, and whether products of suitable quality were available locally or had to be imported. In the United Kingdom, crown glass remained available at least until 1832. Nowadays, sheets for replacement in ancient buildings and for making modern stained glass are still made by the cylinder technique because it remains the only method economically viable for small quantities (by industrial standards) of colored or special clear products. The Verrerie de Saint-Just in France, Lamberts in Germany, Spectrum in the United States, and many other companies are well-known suppliers of these glasses.

2.3 Glass Compositions

The geographical distribution of manufacturing sites evolved over the centuries. Early glassmakers had sufficient local wood supplies as their energy source and they used raw materials derived from around the Mediterranean basin, in particular, alkalis derived from the ash of seaboard plants or especially from the Wadi Natrun salt lake near Alexandria where sodium carbonate hydrate [$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2 \text{H}_2\text{O}$, the *trona* mineral usually named *natron* by abuse of language] was extensively mined (Chapter 10.3). From the beginning of our era, the Levant, and particularly the Alexandria area, was the major glassmaking center from which not only exquisite products but also glass ingots were exported around the Mediterranean coast and ultimately into Roman-dominated regions as far as Iberia, Gaul, Brittany, the Low Countries, and Germany. Over time, the technologies of creating products by remelting ingots and recycled cullet spread too and by the first-century CE glassmaking had reached the city of Rome (Chapters 10.3 and 10.5).

While glassmaking suffered from the decline of the western part of Roman Empire, it remained prosperous in the East in Byzantium [12], especially in the form of mosaics, as well as in the lands that became part of the Islamic World. Particularly important from this standpoint was the shortage of natron that took place in the seventh to ninth centuries [13]. Local plant ash thus had to be taken as a substitute, but its composition was not only more complex but also more variable with, in particular, high K_2O contents in wood ash that made glass more prone to weathering. To the west, increasing fuel pressures in addition meant that glassmaking skills slowly

extended inland along major river systems such as the Po, Rhine, Vistula, and Danube with their wooded valleys [3, 4]. But these changes in glass production also led to important changes in the batch. Wood ash, particularly from beech trees, became the principal source of flux. A significant fraction of the glasses made were consequently more potassium rich.

The changes in the location of glassmaking over the centuries, the use of different raw materials according to availability, the international nature of trade, the recycling of older glasses, and ongoing improvements in technology have all contributed to a considerable variability in glass window compositions (Table 1). Superimposed on these real variations are measurement inaccuracies, which have been extensively investigated in recent years by round robin surveys, for example, by the Technical Committee 17 of the International Commission on Glass (Chapter 10.5), one outcome of which has been the creation of international reference samples. Many analytical techniques (Chapters 2.2 and 2.3) have been applied to determine both major and minor element concentrations in archaeological samples with the goal of increased understanding of provenance and glass production methodologies. These include (Chapter 2.2): X-ray fluorescence (nondestructive, handheld equipment is available, see Chapter 10.1); electron spectroscopy for chemical analysis (ESCA); secondary ion mass spectrometry (SIMS); ion beam spectrochemical analysis (IBSCA); neutron activation analysis (NAA), and Auger emission spectroscopy (AES).

Overall composition, the presence of minor elements, and isotopic ratios are all used to develop an understanding of historical trends and can provide information on the provenance of windows from individual ancient buildings and the raw materials used in making them

Table 1 Chemical compositions of some medieval stained glasses.

	Modern soda-lime-silica glass (%)	Roman glass (%)	Canterbury Cathedral 12th c. (%)	York Minster 12th c. (%)	Blunden's Wood Glasshouse 14th c. (%)
SiO_2	73.6	67.0	54.3	61	58.4
Na_2O	16.0	18.0	1.4	2.5	2.5
CaO	5.2	8.0	16.9	15.8	13.1
K_2O	0.6	1.0	13.7	5.3	11.3
MgO	3.6	1.0	4.2	7.7	6.7
Al_2O_3	1.0	2.5	1.1	2.2	0.9
Fe_2O_3	—	0.5	0.4	1.3	0.7
MnO_2	—	—	0.83	7.7	1.1
P_2O_5	—	—	4.8	4.1	2.0

Source: Data published by the Corning Museum of Glass and adapted by A. S. Meek. University of Nottingham and I. J. Merchant, University of Sheffield.

Table 2 Chemical compositions of medieval window glasses in present-day Belgium from different periods, wt %.

	High potash			High-lime, low-alkali (HLLA)	
	13–14th c.	15–17th c.	18th c.	12–14th c.	15–17th c.
SiO ₂	48 ± 3	56 ± 3	67.3 ± 0.5	47–56	58–61
Na ₂ O	0.5 ± 0.4	1.8 ± 0.9	2 ± 2	0.5–1.0	0.7–3
CaO	22 ± 2	16 ± 2	10 ± 1	23–28	21–22
K ₂ O	21 ± 5	13 ± 2	19 ± 1	7–12	4–7
MgO	3.5 ± 0.4	5.9 ± 1	0.06–0.08	3.7–4.3	3.0–3.8
Al ₂ O ₃	1.5 ± 0.8	1.8 ± 0.7	0.9 ± 0.4	3.1–3.7	3.0–3.9
Fe ₂ O ₃	0.5 ± 0.2	0.7 ± 0.2	0.13 ± 0.02	0.7–1.1	0.9–1.0
MnO	1.1 ± 0.5	1.1 ± 0.7	0.1 ± 0.2	1.2	0.7–0.9
P ₂ O ₅	1 ± 2	2.6 ± 0.8	0.1 ± 0.1	2.1–2.7	2.1–2.6
Cl	0.1 ± 0.1	0.3 ± 0.1	0.1 ± 0.1	0.02–0.2	0.2–0.5
SO ₃	0.4 ± 0.3	0.2 ± 0.2	0.2 ± 0.2	0.2–0.3	0.2

To be compared with the Mediterranean tradition of high soda and low potash exemplified by the compositions of thirteenth century panes in a rose window from Siena cathedral, namely, 56–64 wt % SiO₂, 13–14% Na₂O, 9–10% CaO, 2.5–4% K₂O, and 4% MgO.

[e.g. 14, 15]. In an electron-microprobe study of window-glass fragments [16], including many stained glass pieces from twelfth to eighteenth century Belgian archeological sites (Table 2), the 500 specimens were statistically grouped into five categories: high-lime, low-alkali (HLLA) glasses, three groups of high-potash glasses, and just a few high-soda glasses corresponding to specialist applications (e.g. mirrors). Stained glasses were more often in the high-potash group but not limited to it. Significant trends were: (i) an increasing silica content over time linked to changes in the sand to ash ratio used in glass melting from 1 : 2 to as low as 1 : 1; (ii) an increase in the K₂O : CaO ratio in the fifteenth to seventeenth century, suggesting a change in the fluxing agent and possibly the deliberate use of limestone; (iii) total alkali remaining constant even though the K₂O : Na₂O varied; (iv) the use of NaCl as a flux in later HLLA glasses; (v) higher MgO levels in the fifteenth to seventeenth-century compositions.

For comparison, the chemical composition of some medieval colored stained glasses from the (Cathedral) in Siena, Italy, are given in Table 2 [17]. They have much more soda and less potash and lime than the Belgian compositions, related to the different choice of alkali source as a flux for glassmaking in the Mediterranean area.

3 Social Context

Glassmaking continued during post-Roman (Byzantine) times for the next 500 years on a reduced scale. Few buildings constructed during this period have survived with

their glazing intact but, based on glass fragments recovered from excavations, colored glass panes were being used decoratively during the first millennium. Some were simply assemblies of regularly shaped pieces held in place by leading; this allowed larger windows to be glazed using small pieces. Actually, much architectural attention was paid during the first millennium to maximize the benefits of the light streaming through these windows in large buildings [1].

Images could also be created. An example in the United Kingdom was the church built at St Peter's Monkwearmouth (founded in 674 CE) by Benedict Biscop (~628–690) who went to Gaul to bring “some masons to build him a church in the Roman style,” as reported by his monk Bede the Venerable (~672–735), and then sent “messengers to Gaul to fetch makers of glass (more properly artificers) [...] that they might glaze the windows of his church” [18]. These windows have been interpreted as embodying the image of a simple figure created entirely by joining small colored sheets; none showed any indication of painting. More important, however, is that after the collapse of the Roman Empire, the Church helped to preserve these ancient skills and reintroduced them where they had been lost.

At the beginning of the second millennium, the economic, demographic, and political expansion in Europe led to an expansion in religious buildings of all sizes as witnessed by the numerous abbey churches and cathedrals from the eleventh century still extant. This growth stimulated the development of decorative glazing from its primitive beginnings. The wave of major construction projects was a seed bed for developing new skills. At this juncture an influential figure was the powerful Suger

(1081–1151), abbot of Saint-Denis, north of Paris, and adviser to the French king. Although large windows had already been made, for instance, in Bavaria at Augsburg (Figure 3), Suger gave them a special importance when he rebuilt his abbey church around 1135. In the ninth century, the patron saint of the abbey (a second-century martyr) had been wrongly identified with a sixth-century Greek mystical theologian who was himself assumed to be a first-century disciple of the apostle saint Paul and had taught that light was the vehicle by which the divine was perceived. Suger thus took advantage of extensive reglazing to teach about Old Testament “Types” of Christ and link them to New Testament incidents. Interestingly, he gave a prime panel spot at eye level, which thus served as an advertising space, to the craft guilds that financed a window, no doubt helping to defray the huge costs incurred.

The glass of abbey and cathedral windows was produced by independent manufacturers and sold via a middle man to the artists who turned it into the works of beauty we see today. It was never cheap. This meant that the later art of decorating the panes by painting not only became itself a highly valued skill but also resulted in extensive reuse of the materials themselves. One notable example is the famous window *Notre Dame de la Belle verrière* in Chartres cathedral, which had survived the devastating 1194 fire of the previous Roman edifice (Figure 4). Likewise, twelfth-century panels from a demolished section of York Minster were reused in the fourteenth-century nave in spite of the improvements in design between these periods.

A major change was then taking place because the use of buttresses in gothic edifices for supporting high walls made much larger openings possible, which could thus be extensively glazed in harmony with the bulk of the building [1]. The new feature was most dramatically illustrated by the 640 m² of stained glass installed in the 15.5 m high windows of the Sainte Chapelle, built in Paris from 1243 to 1248 to host relics of Jesus’ Passion such as True Cross and Crown of Thorns. This change gave the possibility of telling an extended story rather than simply teaching through a single image. Now the church wished its congregations to be instructed in its faith. Church Laws also encouraged adding images of Christ and the Saints, particularly those to whom the building was dedicated (Figure 5). This included statues, altar cloths, and screens but was particularly evident in window decorations.

The Black Death brought a temporary halt to the expansion of cathedrals throughout Europe, in the fourteenth century. Once it was over, however, major workshops rapidly developed again, often near major religious centers such as York in the United Kingdom, and an international trade flourished both in finished



Figure 4 The ancient red panels of *Notre-Dame de la Belle Verrière* of Chartres (ca. 1180) reinstalled in a larger window of the early thirteenth-century gothic cathedral. Lower panels to be read from bottom to top and left to right, depicting the Three Temptations of Jesus by the devil (pictured as a beast) and The Wedding at Cana. The light blue of the original panel and the subsequent darker hue reflect a change in the cobalt source used. *Source:* Photo P. Richet.

windows and also in skilled workmen. But a major event in the early sixteenth century was the Protestant Reformation, which challenged throughout Europe tenets of the then current theology. A consequence was the extensive destruction of windows (along with statues, retables, or paintings), which were thought to foster idolatry; fortunately, many were saved simply because their replacement would have been too costly. The new windows made in the seventeenth and eighteenth centuries were thus made to bring as much light as possible to help reading of the Holy Books and watching the priest who celebrated the Mass. New stained glass windows were thus rare, with fresh designs that could be commissioned by either side of the debate to make their point (Figure 6).

As Europe became a safer place, beyond the ecclesiastical community, the gentry too were able to construct larger mansion houses with an increased proportion of



Figure 5 Jesus' crowning with thorns: the most important stained glass panel of the Sainte-Chapelle, in Paris, built to host relics of this crown. In all, 1113 scenes of Scripture depicted in the chapel, only five hues were displayed, namely, blue (cobalt), red and green (copper), yellow (antimony), and purple (manganese). *Source:* Photo P. Richet.

windows. It became the fashion to decorate them too, for example, with the coat of arms of the occupants. Large public buildings also followed similar practices.

4 Glass Decoration

4.1 Body Coloration

Whereas the aim of many early glassmakers was to achieve the ultimate in transparency, those working for architectural applications knew how glass could be colored by the addition of various kinds of *earths*, i.e. what are now termed metal oxides (Chapter 6.2, [19]). From the Roman period onward, body-colored sheets had already been made whereas the Greeks were coloring glass tiles in their walls to create mosaics. Old recipes had thus long been available to color glass, including those of glazers and enamellers whose range of colorants were similar (Chapter 10.8).

Early windows were small and had to provide adequate light levels. Nevertheless, by the twelfth century, church windows already included strong reds and blues. As the proportion of glazing increased, more light entered the building, giving glassmakers the opportunity to experiment with the concentrations of their “pot-metals” to create stronger colors. Interestingly, in medieval United



Figure 6 Noah's ark: a well-known Biblical scene pictured in Saint Étienne-du-Mont church in Paris at the beginning of the seventeenth century, at a time when little new stained glass was made. *Source:* Photo P. Richet.

Kingdom, colored glass sheets were sold by weight rather than by area and at twice the price of clear glass because the latter was of English origin and the former imported.

The oldest surviving windows are notable for the dominance of blue among the colored panels. An early colorant was cobalt ore (Chapter 6.2), which gave rich blues although the source of suitable material was limited. Depending on place and period, the blue glass created by the Egyptians relied on cobalt from local sources or imported from Iran and other areas. A similar substance called *zaffre* (Arabic for cobalt oxide) was extensively used in cathedral glass. An early source of this colorant, also known as Damascus pigment, was the Levant. Later, Saxony became a major supplier, in agreement with the fact that the term *smalt* designating cobalt-rich glass probably derives from the proto-German *smaltian* (to smelt). These ores could not be used directly for melting because they contained mixed cobalt sulfides and arsenide. They required pre-treatment to remove the sulfur and arsenic by volatilization and leave cobalt oxide [3].

Another source of cobalt was the residue from bismuth extraction.

Copper was widely refined by the metallurgical industries of the Roman period, which meant that copper-rich ore was readily available to glassmakers after appropriate processing. From its color, one can guess that such a source called *ferretto* was primarily cuprous oxide. Oxidized brass fillings were also used. As had long been familiar to Egyptian and Mesopotamian glassmakers, copper can color glass turquoise blue or green in its oxidized form [Cu^{2+}] depending on the composition of the base glass (Chapter 6.2). Iron oxide too can impart a pale blue hue to the glass if melted with a reducing flame so that the iron is predominantly in a reduced state [Fe^{2+}]. Mixtures of Co, Cu, and Mn are also common in blue glass, no doubt partly because of difficulties of separation in ancient times but primarily to produce a wider range of blue tints (Figures 3–5).

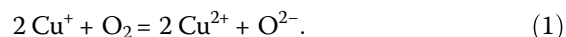
Iron oxides were difficult to avoid completely in the raw materials. They could usefully add a tint to the glass ranging from blue [Fe^{2+}] through green to yellow [Fe^{3+}]. Indeed, one could produce amber colors by melting glass under reducing conditions when sulfur was also present.

Empirically, Romans (Chapter 10.3) already knew the glassmaker's soap. We now understand that it was dissolved manganese, which acts as a decolorizer at low concentrations, reducing the green coloration normally present as a result of iron impurities by oxidizing ferrous iron [Fe^{2+}] to ferric iron [Fe^{3+}]. At higher 1–3 wt % concentrations, though, it colors glass purple [Mn^{3+}]. But solarization is an issue when high manganese concentrations are used as a decolorizer because the UV radiation in sunlight can reverse the oxidation of iron caused by the added manganese. Clear Mn^{2+} then becomes the purple chromophore Mn^{3+} . Glass that has been covered by leading and protected from sunlight can be a good indicator of the original color of a glass sheet and may be observed while a window is being repaired. Glassmakers might even have realized that additives such as arsenic and antimony salts added primarily for removing bubbles (refining) could influence the colors obtained, a phenomenon now understood in terms of a change of the balance of redox ions (Chapter 5.6).

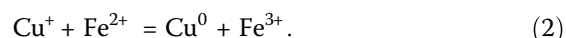
Whereas blue was dominant in earlier church windows, over time the proportion of red increased (Figures 3–5). Ancient glassmakers had already discovered that a copper-containing glass melted under what is now termed reducing conditions can acquire a deep and intense red coloration (Chapter 6.2). The colorant in this case was precipitated cuprite (Cu_2O) or copper metal nanoparticles, which are both so strongly absorbing that, as discussed in the following paragraph, usually a thicker clear layer was combined with a strongly colored thinner layer to allow sufficient light transmission.

4.2 Casing/Flashing

Glass colored red by copper nanoparticles is so deep in color as to be opaque (Chapter 6.2). In a context of great symbolic significance since the red color was the symbol of Christ's martyrdom, two ways were successively followed to obtain the thin red glass required for light transmission. Both were unknowingly relying on two redox reactions [20]. In the first reaction, the virtually colorless cuprous ion is oxidized into the pale blue or green cupric ion:



In the second, the cuprous ion is in contrast reduced to copper metal by electron exchange with other ions such as the Fe^{2+} present in trace amounts:



In a process used from the twelfth to the fourteenth century, which did not have any precedent in the glass-making tradition [20], alternate layers of high- and low-Cu glasses, not always parallel to the surface of the glass sheet, were formed and produced close to their boundaries, within the latter layers, Cu^0 -rich, μm -thick red striations (Figure 7a). The process likely required first

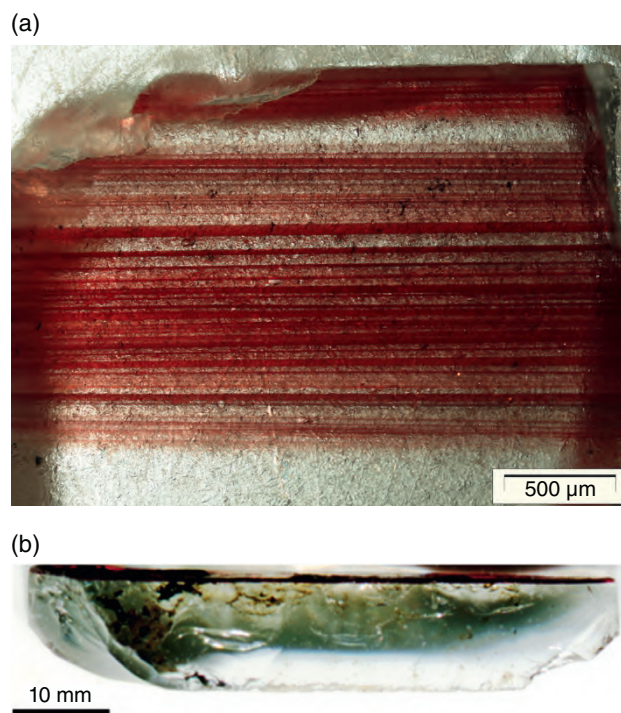


Figure 7 The two processes for producing a red color with copper nanoparticles in Amiens cathedral (northern France). (a) Cross section of thirteenth-century striated fragment. (b) Cross section of a nineteenth-century transparent glass overlaid with a thin, strongly colored red layer, duplicating the simpler process used from the fourteenth century. Source: Photos Philippe Colombar.

the interlayering (without mixing) of a pale blue or green, oxidized Cu-rich glass and a colorless, reduced Cu-poor glass, which were heat treated to let Cu^+ diffuse into the latter to be reduced according to Eq. (2) and to nucleate the Cu nanoparticles; a gather of white glass was then dipped into the interlayered melt and blown to yield a cylinder of white glass coated by the mixed Cu glass in which the layer interspacing was large enough to ensure a ruby translucent effect [20].

From the fourteenth century, another process was used for unclear reasons, but perhaps related to changes in glass composition or a preference for a simpler, more reproducible, and less costly process. A gather of white glass was directly dipped in a pot of Cu-bearing glass so casing the clear glass before blowing. The cylinder formed was opened and heat treated to nucleate and grow the Cu nanoparticles in a 10–300 μm thick red coating (Figure 7b). This method subsequently developed into more sophisticated approaches such as blowing a thin bubble of colored glass and then a second thicker bubble of clear glass inside it, a process termed *flashing*. Such two- or even multilayered glasses might show color variations across a sheet that could be used by an artist to create an effect of light and shade. This effect could be enhanced by etching or grinding away sections of the glass to lighten the color in one area (Figure 8). Such techniques were used by later artists, for example, to create the whites of the eyes of a red demon. Occasionally, other colors, particularly the strong blue of cobalt, were treated in the same way.

4.3 Enamels

Enamels are colored glassy coatings deposited onto smooth surfaces (Chapter 10.6). Their use on clear white glass developed in seventeenth and eighteenth centuries when window glass attempted to replicate canvas painting. They were fired on and melted to a fully glassy, transparent state (Figure 9). Often, large painted rectangles were leaded together or mounted into a metal frame to create the finished window.

4.4 Painting

When leaded together to create an image, individual body-colored sheets have serious limitations in the detail that can be achieved. Painting dark lines onto the colored glass surface solved the problem simply by modulating the amount of transmitted light since the painted areas remained opaque after firing. Termed *grisaille*, the paints used were a compound of ground glass and metal-oxide black pigments (generally, iron oxides) mixed with carefully selected liquid binders to allow the buildup of successive layers prior to firing at around 600 °C or higher



Figure 8 Red flashing on a clear glass, etched away to give the detailed patterning of the costume, along with yellow and red stripes obtained from colored rods deposited on the base glass and drawn upon blowing. Weathering apparent at several places, in particular at the junctions with lead. Detail of the *Crowning with thorns* window (ca. 1470) in Sainte-Madeleine church, Verneuil sur Avre (Normandie, France). Source: Photo P. Richet.

for the image to become permanent (Figure 10). The firing furnace would take several hours to heat up and longer to cool. For this reason, and also to reduce the risk of fracture, the number of firings was kept at a minimum for any one piece of glass. This limited reaction time resulted in a significant chemical heterogeneity, the presence of voids, and thermal expansion mismatching, however, which makes this material bearing elements such as iron, manganese, and lead highly reactive and, thus, prone to corrosion (Figure 11).

This technique goes back almost as far as the use of a combination of colored pieces since indications of drawing have been found on sixth- and ninth-century fragments coming from buildings, excavated in Italy, France, and Germany [4, 5], some displaying recognizable religious images. From the latter period there is also written evidence of such pictures according to descriptions of



Figure 9 A large fire drawn with *sanguine*, a thin red to warm brown enamel made from hematite and other iron oxides melted with a flux on the glass surface. Detail of *The Sacrifice of the Priests of Baal*, an early seventeenth-century window of Saint-Étienne-du-Mont church in Paris. Source: Photo P. Richet.

pilgrims traveling in Europe [5]. Dating back 900 years, the earliest surviving examples are in the aforementioned Augsburg Cathedral, but their high quality suggests that the tradition of glass painting was already well established.

Although the style of painting and decorative techniques evolved over the centuries, the basics have remained unchanged [21, 22]. Application of paint by a smear technique was the earliest, followed from about 1300 by stippling with a long hog hair brush, and later by the use of badger-hair brushes for smoothing the paint to an even finish (*badgering*). All these techniques served for modeling and were usually applied onto what would become the interior surface of the window although the paint could also be applied to the reverse of the glass for special effects. Trace lines provide basic outlines and shapes, for drapery, hair, faces, etc. For highlights, stickwork cut back through the paint layers to the base glass.

4.5 Silver Staining

As introduced from the early fourteenth century, an easier method producing a yellow hue on a single sheet of clear glass was silver staining. The technique was



Figure 10 Grisaille work in a sixteenth-century panel from a church in Chartres destroyed during the French revolution, which is now exhibited at the Centre International du Vitrail in Chartres. Source: Photo P. Richet © C.I.V.

similar to that developed for luster pottery by Abbasids potters at Baghdad and Samarra during ninth century, some records suggesting that it already existed in the Roman/Byzantium Empire [23]. This development was accompanied by a significant growth in the output of decorative glass. A stain made up of clay or Venice turpentine containing silver compounds such as the nitrate, chloride, or sulphate is deposited on areas of the image such as the braiding of a rich costume, the halo around the face of a saint, or a golden crown where a yellow color was appropriate (Figures 12 and 13). The concentration of silver metal precipitated in the glass is limited by the glass composition (redox ions present) so only low concentrations of silver in the stain are needed. To deepen the color, up to three or four painting and firing cycles may be used to increase the depth of penetration; and so to control the shade of color produced, which can range from straw yellow to dark orange. To avoid the use of extra leading, the same process carried out on a blue glass may produce the

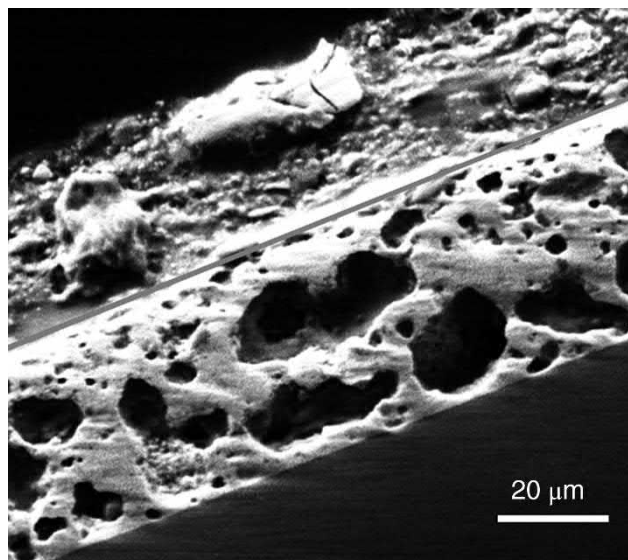


Figure 11 The heterogeneous structure of grisaille revealed by scanning electron microscopy. White line drawn to distinguish its surface from its section. *Source:* Micrograph Philippe Colomban.



Figure 12 Silver staining: yellow shading in the church of St Thomas, Eccleston, on the “little maid” from the story of Naaman, by Horatio Walter Lonsdale, a noted glass artist in the late 1890s. *Source:* Photo David Martlew.

green color, for instance, needed to represent foliage (Figure 13).

Upon firing, four successive steps have been distinguished [23]: (i) penetration of Ag^+ within the glass through exchange with alkali ions; (ii) diffusion of Ag^+ deeper below the glass surface as determined by Fick’s law; (iii) reduction of Ag^+ into Ag^0 either by oxidation of Fe^{2+} or other ions or by reaction with non-bridging oxygens; (iv) aggregation of insoluble Ag^0 into silver nanoparticles, which may themselves coalesce. Staining is carried out below the transformation temperature of the glass



Figure 13 The smart integration of thin leading to delineate tree trunks: details of the heavily restored sixteenth-century stained glass window depicting Abraham and Melchizedek in Sainte-Foy church, Conches-en-Ouche (Normandy, France). Silver staining at the bottom. *Source:* Photo P. Richet.

and at a lower temperature than that needed for firing on paints. At higher temperatures, some silver can diffuse back to the surface creating a reflective layer. Staining is, therefore, the last process to be undertaken in creating an image. The color obtained and its uniformity markedly depend on the starting silver salt and firing temperature: an intense color is, for instance, obtained with AgNO_3 and Ag_2SO_4 fired at lower temperatures, but is homogeneous with the former salt and not with the latter [24].

5 Leading

The production of a stained glass window begins with a drawn image incorporating lead lines. In medieval times, this would have been done on a whitewashed table of

which the fourteenth-century Gerona table is a surviving example [5]; as paper became more available and its cost fell, a full-size image or “cartoon” would have been drawn on this medium. Pieces of glass were cut to the shapes and the artist, who may or may not have been the designer, then paints the detail on the blank glass, following the lines on the drawing. These cartoons were often reused, sometimes reversed. Some stained glass designs were inspired by or copied from printed sources or canvas painting; some firms maintained a pattern book as a basis for their creations.

Initially, glass windows were set in frames of wood, plaster, or even bronze. As the images increased in complexity, ways of assembling multiple pieces of glass into a stable structure were needed. To hold different sheets together, the method adopted over many centuries has been to use a lead strip, termed *came* (from the Latin *calmus*, reed), with an H profile. Not only does lead have the advantage of melting at the low temperature of 327 °C, but it is a soft material that deforms readily and, thus, adjusts to the shape of the glass panes while preventing stress from accumulating at their edges. The original comes were probably made by pouring molten lead between parallel reed stems on top of sand contained in a bottomless wooden box. Upon casting, the reed stems burnt away, leaving a flat slab of lead containing parallel holes. Cutting along the holes with a knife finally yielded an “H” section strip of lead. From the seventeenth century, the came has been obtained more directly by extrusion with a full width that now ranges from as little to 2 mm for subsidiary lead lines to 20 mm, 6 mm being the norm for the main lines. Alternatively, the came profile can be square but bending them is more difficult than with a convex profile.

Leading highlights the outline of the image being created. It has always been carefully integrated into the image design, sometimes in the form of thin lines (Figure 13). In this respect, its role is similar to that of the painted lines used by the artists. Although a key development in the technology of stained glass, its origins are unclear. One pointer is that scraps of lead have been found with glass fragments from Roman buildings in both Germany and France. An early development in producing decorative designs with this technique was the use of glass quarries, square- or diamond-shaped pieces of single- or multicolored panes assembled into diagonal lines in patterns that have remained in use to this day. This technique allowed large areas to be glazed with the small panes that could be easily made from crown glass.

To create an image, the individual glass sheets had to be cut first into more complex shapes. The glazier had several tools at his disposal, which have not changed much over the millennium. The medieval glazier broke the

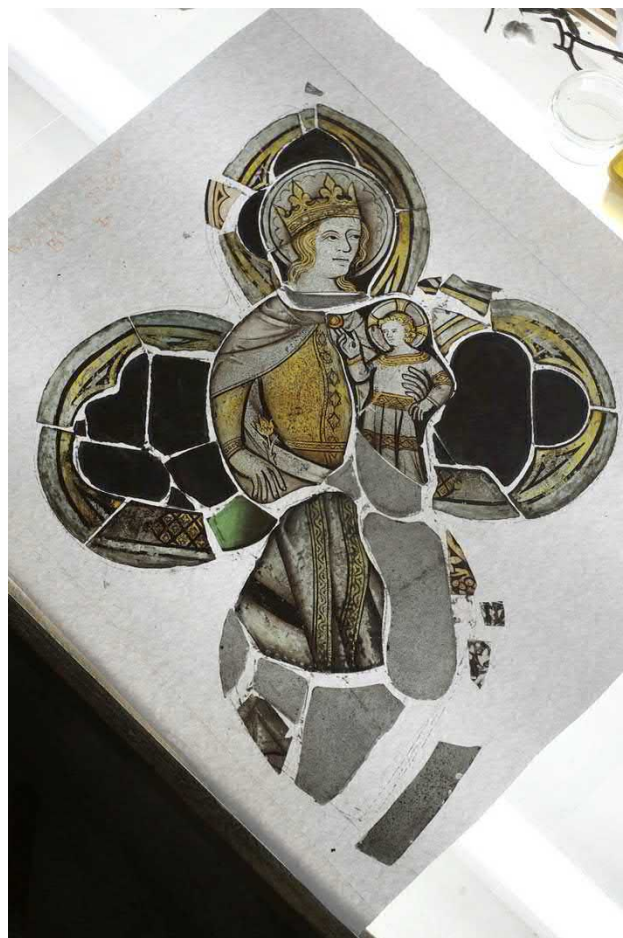


Figure 14 Restoration of an English fourteenth-century stained glass window in the parish church of Wycliffe, St Mary the Virgin (Diocese of Leeds) after a catastrophic fire. Individual fragments assembled after cleaning, ready for leading. *Source:* Photo John and Ruth Cooke.

sheets into smaller sections with a red-hot iron. Finer detail was obtained with a grozing tool, pliers, or a simple strip of metal with a square notch at one end to grip the edge of the glass and “nibble” away small fragments of material. The glass-cutter with a small rotating wheel of a hard mineral (nowadays steel or tungsten) is a relatively modern development. Diamond cutters have also been used to score the glass for initial shaping.

Cutting the colored sheets was facilitated by a life-size cartoon depicting the intended image. Once each piece was completed, it was laid out on the glazing bench (Figure 14), the leading was added, and finally joins in the came were soldered into place to create a water-tight window. Actually, the leading itself was part of the overall design of the picture, serving in particular to separate differently colored sheets (Figure 13). The glazed and leaded panels had then be installed, supported by a configuration of stanchions and horizontal wrought iron



Figure 15 Exterior view of a thirteenth-century stained glass depicting Christ's Passion in the choir of the Sainte-Chapelle, in Paris, held in place by *ferramenta*. Panel not cleaned, having kept the patina (mixture of gypsum and oil + dust) deposited at the time of the restoration made between 1846 and 1855 by F. Duban, J.-B. Lassus, and E. Boeswillwald. *Source:* Photo Philippe Colomban.

bars, or *ferramenta*, built into the surrounding masonry (Figure 15), but also generally visible from the interior (e.g. Figures 2–8).

6 Later Trends: Nineteenth to Twentieth Century

Following a period of relative dormancy, the renaissance of Gothic Architecture in the eighteenth–nineteenth century created a revival in stained glass windows especially in England where the 1818 *Church Building Act* resulted in the construction of about 600 churches in the new urban centers that were rapidly expanding. Many of the artistic effects/glass technological developments that had peaked in the Middle Ages had to be reinvented. But the continuous increase achieved in the meantime in glass quality was in itself problematic because advantage could no longer be taken of defects to produce special effects such as the scattering of light by tiny air bubbles. One-time director of the Chance Brothers glass-making company, Georges Bontemps (1799–1883) was one of the foremost pioneers in the reconstitution of ancient processes (Chapter 10.9) but his own work in stained glass was definitively in the new, distinctive style of the nineteenth century (Figure 16).

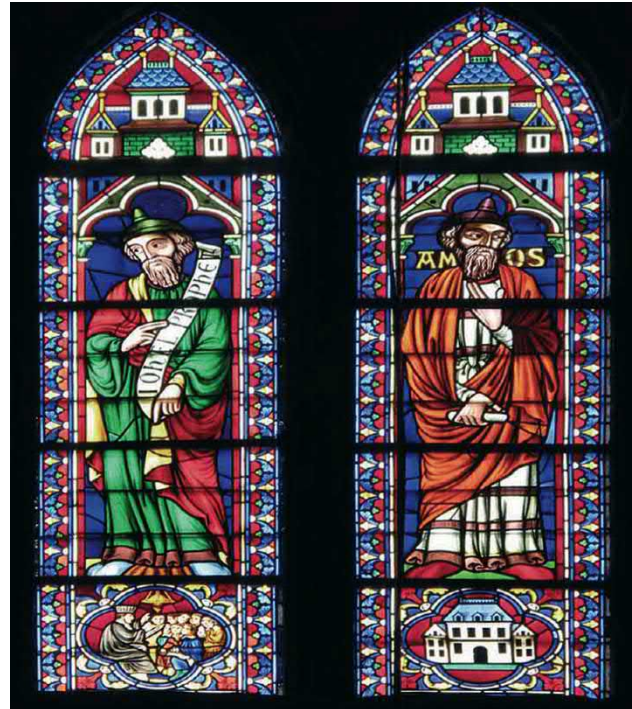


Figure 16 The prophets Joel and Amos of the Old Testament pictured by the famous glassmaker Georges Bontemps (Chapter 10.9) in the basilica Notre-Dame de Bonsecours, near Rouen. Hues much darker in the nineteenth century than in the Middle Ages. *Source:* Photo Danielle Velde.

In a context where a high level of artistry had been regained, the period was in parallel characterized by increasing experimentation in glassmaking for decorative purposes. The situation created significant tensions in that the church, which still remained a major patron of the field, often had an approach limited by the constraints of a past grounded in Gothic Architecture (Figures 16 and 17). The Arts and Crafts movement generated a desire to return glassmaking to its early roots. Consequently, another method of making sheets used by the Romans was reintroduced in 1889. The approach was to blow a square bottle and then use the sidewalls and base as sheet glass. A characteristic of this product was that the middle of each face was much thicker than the edges. Sheets were sold as *Prior's Early English* or *Norman* slab glass and were often brightly colored.

In England, the influence of Augustus and Charles Pugin was very important in the 1830s. Great effort went into the methodologies for making suitable sheet glass. Several firms arose throughout Europe to reproduce the earlier techniques. For example, in the United Kingdom in the 1840s, Winston used chemical analysis in an attempt to uncover the secrets of medieval windows. A key firm in the United Kingdom was James Powell and Sons of Whitefriars Glassworks in London. The



Figure 17 Late nineteenth-century stained glass from Christ Church, Eccleston, St Helens, created by the famous Hardman studio in Birmingham in 1885, which became well known in 1838 when it was commissioned to make the ornamental metalwork of the new Houses of Parliament in London. Source: Photo David Martlew.

output of such firms was used both in the restoration of much older stained glass and the creation of new windows for the rapidly expanding number of churches during the nineteenth century with architecture influenced by the Gothic Revival. These artists though were willing to adopt new approaches not widely used previously such as the acid etching of flashed glass or adding colored glass to provide surface texture [25]. Artists thus obtained special effects by combining the newly rediscovered ancient techniques with processes used in other fields, such as the porcelain transfer printing or with the wholly new invention of photographic impression [26].

During the same period, the Americans made a particular contribution to the decorative glass market by applying similar techniques to lamp shades and similar items. The most famous of these was Louis Comfort Tiffany (1848–1933). By mixing several different colored glasses into one sheet and adding small fragments of colored glass to white glass, he created a wide range of impressive optical effects, which became very popular. These were assembled in the same manner as traditional stained glass, substituting copper foil for lead came.

The early twentieth century also saw a step change in the artistic world as a revolt against the strict formalism of earlier years, which gave rise to the Art Nouveau movement. As exemplified by CdS–CdSe solid solutions, the discovery of new pigments allowed a vivid coloration to be combined with a high luminosity for color ranging from yellow to red [27]. Controlled nucleation of these new semiconductor nanoparticles upon processing of the glass piece thus replaced the ancient techniques based on silver and copper metal nanoparticles.

These new processes spilled over into stained glass in part because many eminent artists like Jacques Grüber (1870–1936) were commissioned to create decorated glass windows. Images were increasingly influenced by nature with its inherent colors and curves. As glass art ceased to be primarily the domain of the church, the images created became increasingly secular in content. Many artists, for example, Charles Rennie Mackintosh (1868–1928) in Glasgow, introduced more abstract designs while other famous artists such as the painters Henri Matisse (1869–1954) and Marc Chagall (1887–1985) also committed themselves to stained glass.

More recently, several new approaches have been used at the same time as glass art expanded into new directions. These rely, for instance, on *Dalles de verre* (Glass slabs) or combinations of different industrially produced clear and patterned glasses, an example being slabs up to 5-cm thick whose varying texture makes it possible to use them unpainted in the creation of giant mosaics. Cement or resins replaces the leading used earlier to hold the pieces together (Figure 18). Modern developments in cutting technologies with water jets or laser beams has allowed the production of complex shapes that can be joined simply and accurately along their edges by modern adhesives, for example, UV-cured resins. This method allows images to be produced without leading; the resins can, however, discolor under the action of UV light over longer periods. Another approach is in effect to create a collage by joining or fusing colored and clear sheets together. It is even possible to use coarse powdered glass remelted at relatively low temperatures in the *Pâte de verre* (Glass paste) technique to keep air bubbles and other heterogeneities as decorative elements (Figure 18).

Production technologies have also changed dramatically (Chapters 1.4 and 10.9). From the early twentieth century, machine-drawn glass sheets displaced the old cylinder- and crown-glass production for many architectural applications. The earlier Fourcault process was supplanted by the Coburn process in the 1920s, but the best was the PPG Pennavon process invented in America and perfected by Pilkington in 1933 (Chapter 1.4). Now, float glass is the dominant product on the market. Such glass lacks the optical variability of earlier products, giving almost perfect reflections and transmitted images; many



Figure 18 Stained glass made from *Pâte de verre* panels held by cement (d. 133 cm): Christ and the children pictured in 1934 by François Décorchemont (1880–1971) for the Sainte-Foy school of Conches-en-Ouche (Normandy). Source: Photo Musée du verre de Conches/Siloé, courtesy Éric Louet (inv. MV.1993.1.1).

would argue that something has been lost and certainly such products cannot be used for repairing ancient windows. However, one approach that has been used with some considerable success is to add engraved images to such sheets as a new way of creating decorative windows.

7 Conservation

Corrosion is not a new concern for glass (Chapters 5.11 and 5.12). The sand used as a raw material by early glassmakers in the Levant had adventitious concentrations of calcium oxide from sea shells, which ensured the stability of their products. As a flux, naturally occurring alkali-rich material such as the natron found in Wadi Natrun was particularly appropriate (Chapter 10.3) and traded for making other commodities such as dyes or unguents. After the Roman times, the “Alexandrian” glass made with this flux was no longer available in Europe where the ashes of plants growing in maritime environments, such as *salicornia*, became used as a flux after concentration by washing and evaporation. These soda glasses with added lime were relatively durable so that ninth-century window glass excavated from an early site in Jarrow, Northumberland, United Kingdom, still retains its translucency.

As they moved inland during the first millennium, glassmakers turned to the ash of trees as a fluxing agent, ending up with compositions much richer in potassium (Table 2). For example, Theophilus’ writing in the twelfth century [9] recommended the ashes of beech wood;

bracken was also used. Accounting for more than half the production by the thirteenth century, these potash (*pot ash*) glasses were less chemically durable than soda glasses so that they have survived less well in stained glass windows. Corrosion mechanisms and conservation are consequently significant issues [3, 4]. The problem can be real even for twentieth-century windows; when cement was used in place of lead to assemble the panes, the *basic* environment caused corrosion (Chapter 5.11).

Corrosion typically results in the pitting of the outside surface but can also be significant on the inside of the pane where condensation and evaporation cycles occur, the first drawing out the alkali from the glass and the second concentrating it to produce a strongly alkaline environment, which is particularly detrimental to the glass surface (Chapter 5.11). Enamels that are insufficiently durable can also result in loss of detail over time. Modern conservation aims at reducing this cycle by means of internally ventilated environmental glazing systems whereby the historic glass is protected by a layer of protective glazing and the interspace is vented to the inside [17].

Over the centuries, accidents, fires, and wars have obviously been in many ways more effective in causing damage or destroying stained glass than corrosion by water or animal excreta. Another insidious source of degradation is the displacement of rigid stone frameworks built on clay bedrock that are induced by seasonal changes of the groundwater level and cannot always be accommodated by the lead comes. Upon simple breakage, the easiest way to fix the damage was to add some leading (Figure 19). When destruction was more severe, complete panels were often replaced in the nineteenth century by new stained glass that may look so similar to the original (Figure 11) when templates and detailed drawings were available that distinguishing ancient from recent work can be difficult. The huge optical absorption of Cu nanoparticles particularly caused difficulties in nineteenth-century restoration of medieval stained glass. Replicas of red glasses consisted of a thin red layer covering an optically clear plate (Figure 7b), which was then etched with HF to mimic the heterogeneous nature of medieval pieces (Figure 7a).

Since it has to be replaced roughly every 100–150 years, the leading fails long before the glass. This event allows for some cleaning of the glass and any necessary restoration. Old windows must also be cleaned. An important debate has been the extent to which cleaning and repair should include repainting of images. Over the years, some such restorations, particularly if they have occurred after a catastrophic event such as a fire, may have resulted in confused images. The use of computer technology has facilitated the re-creation of such pictures in the way one would tackle a jigsaw.



Figure 19 An ancient, obvious repair at the head of an apostle in a sixteenth-century panel from a church in Chartres destroyed during the French Revolution, which is now exhibited at the *Centre International du Vitrail* in Chartres. Source: Photo P. Richet © C.I.V.

Stained glass windows, particularly the old ones that need repair, used lead that also contained not only trace amounts of copper or tin but also of potentially dangerous impurities like antimony. Paints and glass colorants contained a variety of toxic materials so that abrading glass creates a dust hazard; acid etching also involves hazardous materials. Hence, all new projects and any restoration work must be undertaken with the associated risks in mind. A useful guidebook has been written on this subject [28].

8 Perspectives

At all periods, stained glass has not been an art in itself but a key ingredient of monumental art. Whereas it was designed to highlight the beauty and harmony of the building in which it was installed, in return the building architecture was designed to give it a privileged place.

With a style that evolved throughout the ages and perhaps reached a formal apex in the sixteenth century when all the technical resources of painting on glass had been mastered, it benefited from new forms of expressions after the eclipse of the seventeenth and eighteenth centuries. As in other branches of the art community, stained glass artists continue to develop new styles and techniques in line with the increasing secularization of their audience and to apply their skills ever more widely in the domestic context. Imaginative abstract images are much more common and even in religious settings designs have been influenced by movements such as cubism and expressionism; the church in France has been particularly open to contemporary designs as exemplified by the romanesque basilica Saint-Julien in Brioude (French Massif Central) recently adorned with new stained glass made by the Korean master Kim En Joong (b. 1940) [29]. New techniques are being developed and old ones reinvented to suit the use of stained glass in new architectural situations such as shopping arcades and for the smaller commissions that are now often the bread-and-butter of the trade [4, 29].

At the same time, the preservation, renovation, and conservation of ancient glass panes form a significant part of the activity of stained glass artists. Accurately reproducing the color and surface texture of old windows imposes its own requirements on them and requires a deep understanding of ancient methodologies in this field. The stakes are especially high as the extant stained glass windows represent but a tiny fraction of those that were originally installed. The destructions wrought by the two world wars are of course familiar, but the massive losses throughout the ages caused by civil wars or the dissolution of monasteries at the time of the Reformation are not so well known.

Of course, the progress made in the last decades in both glass science and analytical methods is being put to good use to investigate the effects of long-term exposure to the atmosphere [30] and atmospheric pollution as well as to determine more accurately the history of the material [14]. At the thirteenth-century Sainte-Chapelle in Paris (Figure 19), portable Raman spectrometry (Chapter 2.2) has, for instance, proven to be a valuable tool to distinguish on site the original 13th material from the glass repairs made in the nineteenth century [13]. Because the high-frequency Si–O vibrations are sensitive functions of the network modifiers present, it is, for instance, possible to distinguish Ca-rich Na-bearing, mixed Na, Ca, and K-rich glasses.

Interestingly, the conclusions derived can be inconsistent with those recently drawn from visual inspection, which is not so surprising since the nineteenth-century restorers had been competitively selected on the basis of their ability to duplicate original stained glass panels



Figure 20 Raman spectroscopy in the service of ancient stained glass: on-site nondestructive measurements made in the Sainte-Chapelle in Paris. Remote optical head mounted on a XYZ stage precise to within 1 μm and connected by optical fibers to an air-cooled green laser and to the engraved prism spectrometer and its CCD detector. Original windows from the thirteenth century picturing Saint John the Baptist and the Book of Daniel, heavily damaged at the bottom during and after the 1789 French Revolution, and restored in a nondocumented way between 1846 and 1855 with either replicas or original pieces taken from the top. Source: Photo Philippe Colombar.

[31]. That medieval techniques were then mastered suggests that glass characterization is needed to determine unambiguously the origin of stained glass when the existence of repairs is known historically. In addition, observations made on the external sides of the panels can give misleading information on ages because surface weathering causes a significant decrease of spectral intensities [32].

As for accurate chemical analyses of the original Sainte-Chapelle glasses, they have revealed that two different sources were used in the same windows, probably because of the unusually high amounts of glass needed to be produced in a short time interval (Figure 20).

Interestingly, both glasses were made near Paris from the same plant ashes but one of them has a typical “Norman” composition characterized by higher Na_2O and MgO contents, which indicates the hiring of Norman masters who were able to add small amounts of NaCl to the batch to lower melting temperatures [15].

If stained glass has much benefited from the advances made in materials science, the reverse is also true, thanks to fragments excavated in generally well-defined contexts. Since these samples differ by their chemical compositions and have been subject to corrosion over many centuries, they represent valuable model systems to determine the long-term stability of glasses under natural conditions. Applications of these studies have thus been made to glasses used to store waste, particularly radioactive material [33].

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10.9

Furnaces and Glassmaking Processes: From Ancient Tradition to Modernity

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1 Introduction

In the first centuries of our era, the importance of glass items in the households of the Roman Empire was such that it would remain unmatched until the seventeenth century. In antiquity, the large scale of some melting tanks – pulled down to recover the melted glass – is indeed well documented in the Levant from where glass was exported throughout the Roman world – and even beyond – either as finished products or as ingots to be shaped in small workshops (Chapter 10.3). Culminating with the invention of blowing and associated decorative techniques (Chapter 10.5), the glassmaking processes devised in antiquity then underwent little changes throughout the ages.

After the collapse of this well-managed system in the early Middle Ages [1], glass had to be made locally from the available raw materials, at a scale that was small by antiquity standards. The furnaces would remain small until the fifteenth century when a marked size increase allowed a number of glassblowers to work in parallel thanks to multiple working ports [2]. Far from the Near Oriental cradle of the industry, a major problem that restricted glassmaking was the lack of adequate local sources of alkali salts. The most convenient sources were the Na-rich ashes of salt-tolerant plants in the Mediterranean and the K-rich ashes of wood, fern, or bracken in Northern Europe, actually complex mixtures of carbonates and other salts that were bearing unwanted coloring elements (Chapter 10.11). For centuries, the so-called *forest glass* was made in local glasshouses with a crude design, greenish or brownish hues, mediocre quality,

and, thus, with walls that were thick and incorporating air bubbles, stones, or other defects.

In Venice, which would dominate the European glass world from the fifteenth to the seventeenth century thanks to the purification process applied to alkali salts, glass working appeared at the turn of the first millennium but significant production began only in the thirteenth (Chapter 10.7). That was the time when stained glass was already made throughout Europe, mainly for church windows, in small workshops with the crown and cylinder processes (Chapter 10.8). Along with economic expansion, further improvements in these processes and glass transparency led to the development of glazing in civil architecture from the fifteenth century. Glass was remaining expensive, however, so that in 1567, the Surveyor of the Duke of Northumberland recommended [3] that

in consequence of the extreme violence of the east winds, the glass of the windows of this and other of the Lord's Castles and Houses in this country do decay and waste, and it were desirable that the whole height of every window at the departure of the Lord, and during the Lord's absence, were taken down and laid up in safety, and at such time as the Lord or any other should lie at any of the said places, the same might be set up anew with small charge, where now the decay is very costly to be repaired.

Such recommendations were hitherto not uncommon, but they rapidly became unnecessary because panes of rapidly increasing sizes were produced at reduced prices, as particularly well exemplified by the large, permanent windows of the Versailles palace in the seventeenth century.

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Technical improvements remained empirical in nature until the end of the following century, in particular when melting of the raw materials had to be changed in significant ways to cope with the replacement of wood by coal in furnaces. As the makers of telescopes and microscopes repeatedly complained, however, glass quality remained problematic for demanding applications because of the presence of bubbles, striae, streaks, veins, tails, and other defects caused by solid inclusions and the chemical variability of the raw materials, which could not be remedied by insufficient melting temperatures and chemical homogenization (Chapter 10.10). As a distant consequence of the Scientific Revolution, the situation began to change rapidly at the turn of the nineteenth century thanks to progress made in both chemistry and physics. The discovery of alkali and alkaline earth elements from soda, potash, lime, and magnesia would of course represent a major starting point to improve glass compositions and control them through quantitative analyses of the raw materials used (Chapter 10.11). Understanding of combustion mechanisms as reactions with oxygen, together with the advent of thermodynamics, and, in particular, the formulation of the notion of *energy* and of the Law of its conservation in the 1830s rapidly had also a strong impact on furnace design and, thus, on melting processes.

The quality of glass and production volumes have always critically depended on melting conditions. Hence, it is appropriate to begin this review with furnaces; the two main points of interest are ways in which higher and more homogeneously distributed temperatures have been progressively obtained and how the switch from pot to tank furnaces took place and eventually made continuous production possible from batch melting to the final glass object. Because plate glass had to be of unusually high quality, it fetched the highest prices and required special fabrication procedures that will be discussed next. Plain flat glass will in contrast be only briefly mentioned because the ancient crown and cylinder methods are described in Chapter 10.8 and the float and previous mechanical processes designed from the late nineteenth century in Chapters 1.4 and 9.6. At the other end of the market, attention will rather be paid to the fabrication of glass containers until the beginning of the twentieth century, the recent part of the story being told in Chapter 1.5. As for safety glass (Chapter 9.2) and fibers for either mechanical reinforcement (Chapter 1.6) or thermal insulation (Chapter 9.3), their production is too recent to be reviewed in this chapter. In preamble, however, it is useful to review the issue of the sources available to understand past processes.

2 The Written Sources

Like for antiquity, extant artifacts and archeological remains are the main sources of information on glassmaking in the Early Middle Ages in view of the lack of written sources for both periods. Although the ancient methods were still used for shaping glass (Figure 1), their first known descriptions date back to only the twelfth-century with the treatise *On Divers Arts* of the Benedictine monk Theophilus [5]. Along with glazing with plain or stained glass, different kinds of furnaces made of stone and clay were described at the beginning of Book II of this treatise. Whereas a large furnace, 15 ft in length and 10 ft in breadth, was divided into three parts for making glass, two slightly smaller ovens were specifically designed for cooling and for dilating and flattening it.

From the Renaissance, the ground is firmer thanks to two famous monographs that differed from Theophilus' work not so much by their technical content than by their woodcuts, which dramatically illustrated the importance of the new printing press for the diffusion of applied knowledge. These books were the *Pirotechnia* [6] of the Siennese metallurgist S. Vanoccio Biringuccio (1480–1539) and the *De Re metallica* [7] written with more detail in Saxony by the former physician Georgius Agricola (1494–1555). There were many reasons why glassmaking was dealt with in these two metallurgical treatises. An obvious one was that, as illustrated by Biringuccio and Agricola's plates, melting furnaces were actually strikingly similar in metallurgy and glassmaking. And not only was in addition glass akin to metals in natural philosophy (Chapter 10.4), but the term *metal* already used in Babylonian times by workers to designate the molten glass (Chapter 10.11) was still in use in the workshop [8] and would in fact remain so until at least the end of the nineteenth century.

It was only from the early seventeenth century that technical treatises especially devoted to glass were published. The most influential was the *Arte vetraria* [9] written in Florence by the priest Antonio Neri (1576–1614). This compilation of recipes for preparing and coloring glass, mostly Venetian, was written in the style of *book of secrets* at the request of the ruling Medici princes who were sharing with Neri a strong interest in alchemy and thought that the remarkable properties of glass were a key component of any attempt made at metal transmutation [8]. As a matter of fact, Neri's recipes were often obscure and addressed the needs not of ordinary glassmakers, but of "a small number of artists and highly skilled artisans engaged in the production of rare and expensive glassware for wealthy princes" [8]. When they translated Neri's book into English [10] and German [11], the physician, botanist, librarian, and founder Fellow of



Figure 1 Glassmaking as pictured in the *Pit of Memnon*, one of the plates of Ms. 21489, British Library, an early fifteenth Bohemian century manuscript illustrating the *Voyage d'Outremer* (the Holy Land), actually a compilation of previous accounts [4]. Except for the extraction of the raw material from a legendary inexhaustible pit at the top of the plate, the picture describes contemporary practice in Bohemia: blowing and marvering of the gob before a furnace made up of a melting compartment at the center and an annealing oven on the left, and heated with wood introduced through the opening at the bottom right.

the Royal Society Christopher Merrett (1614–1695) and the chemist Johannes Kunckel (1630–1703), respectively, complemented it with much additional material. For Merrett, who had been asked by the famous chemist Robert Boyle (1627–1691) to do the translation, like for Neri and Kunckel, glassmaking had been a kind of hobby,

which is probably why Agricola's woodcuts – and not original drawings – found directly their ways into their treatises.

Jean Haudicquer de Blancourt (b. ~1650) was in France an actual glassmaker. His *L'Art de la verrerie*, which also became a reference work at the very end of the

seventeenth century, borrowed also much from Neri while incorporating new recipes as well as alchemical speculations [12]. The fortune of Neri's book nonetheless kept going on in the eighteenth century since a French translation of the German edition, including Merrett's and Kunckel's additions, was published in 1752 by the German-born Paul-Henri Thiry, baron d'Holbach (1723–1789) [13]. Finally, a Spanish translation of this French version was then published as late as 1780 [14] at the request of the king Carlo the third (r. 1759–1788), 168 years after the original publication of Neri's treatise [15].

Although lacking in detail, early patents nonetheless constitute another useful source of information as illustrated by Ravenscroft's on *flint* glass (Chapter 10.10). As a matter of fact, much information on lead-bearing compositions had already been reported by Neri himself who stated, for instance, that the glass of lead "is the fairest and noblest glass of all others at this day made in the furnaces," or that "the pots and Lead must not have too much heat in the furnace neither must be the metal be wrought too hot" ([8], Chapter LXI). By far, however, the most accurate and comprehensive descriptions of all the facets of glassmaking and shaping were written by Antoine Allut (1743–1794) for the epoch-making *Encyclopédie* published by Denis Diderot (1713–1784) and Jean D'Alembert (1717–1783) [16], to which Holbach contributed heavily. Of special interest were the 169 large plates appended to the articles on glassmaking, which still represent the best reference about traditional methods and constitute an extremely rich iconographical resource that has since then been extensively mined (Figure 2).

By itself, the interest raised for so long by Neri's book attests to the slow pace at which glassmaking evolved during the seventeenth and eighteenth centuries. From the early nineteenth century, however, repeated advances resulted in a technical literature that began to include chemical analyses and became rapidly so large that it cannot be reviewed in any detail. Because some of their plates are reproduced in this chapter, only two influential treatises will be mentioned. The first is the rightly famous *Glass Maker's Guide* [17] written by Georges Bontemps (1799–1883), an engineer about whom a glassmaker from the Chance family said that "no one alive knew more than he about every branch of glass manufacture, whether in theory or in practice" [18]. From 1823 to 1847, Bontemps [19] actually directed the glass factory of Choisy-le-Roy, near Paris, and then from 1848 to 1856 the Chance Brothers company in Birmingham where he brought the know-how of the Guinand process for making homogeneous flint glass (Chapter 10.10). As for the second of these reference books [20], it is *Glass, Its History, Its Making* of the chemist Eugène Péligot (1811–1890) known among other achievements for his discovery of the uranium element.

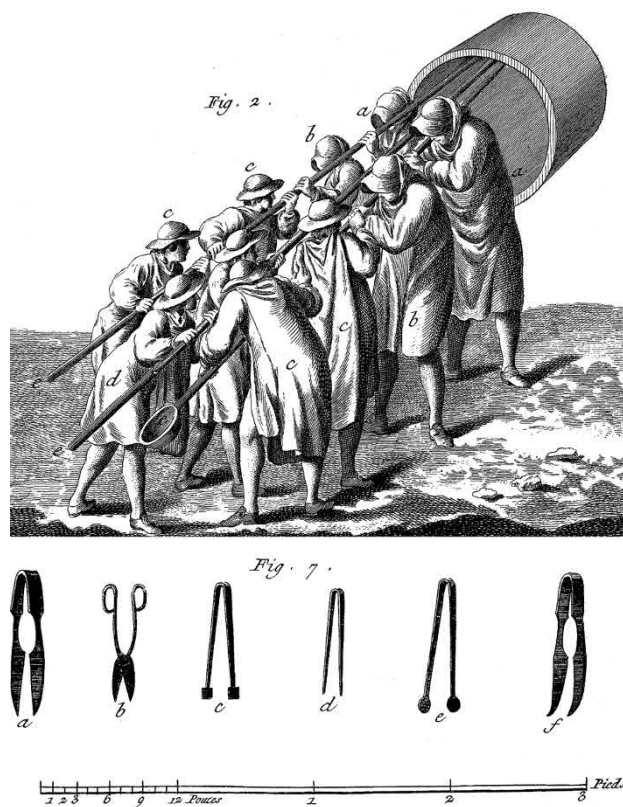


Figure 2 Two aspects of late eighteenth-century glassmaking depicted by the *Encyclopédie* [12]. Fig. 2: The hardship of the craft; the loading of a big melting pot into the furnace by workers turning their back on the fire and protected from the heat by two wet carter's smocks stuffed with straw and clay and wearing double hats also filled with clay. Fig. 7: The working tools of the glassmaker; from left to right, shears (the Roman *forfex*), scissors, and four kinds of tongs (scale in feet).

For later periods and, in particular, the development of mechanization in the various branches of glassmaking, the studies published by Michael Cable (1934–2016) will provide readers with much more detailed accounts than could be presented here [21–24]. Particularly interesting are the blueprints of numerous machines included in these papers, which allow their evolution to be tracked down step by step.

3 Furnaces

3.1 Traditional

As stated by Agricola [7], "some glass-makers use three furnaces, others two, others only one. Those who use three melt the material in the first, re-melt it in the second, and in the third they cool the glowing glass

vessels and other articles.” Reporting the respective sizes of these different furnaces, which were typically from 6 to 10 ft wide and up to 8 ft high (Figure 3), Agricola explained that

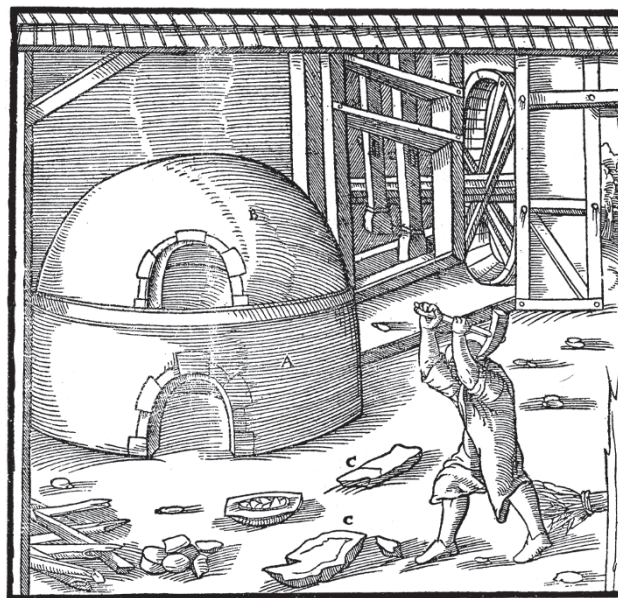
Of these, the first furnace must be vaulted and similar to an oven. In the upper chamber [...], the mixed materials are heated by a fierce fire of dry wood until they melt and are converted into a vitreous mass. And if they are not satisfactorily purified from dross, they are taken out and cooled and broken into pieces; and the vitreous pieces are heated in pots of the same furnace.

The second furnace is round [...] on the outside, so that it may be stronger, it is encompassed by five arches [...]; it consists in a like manner of two chambers, of which the lower one is vaulted [...]. In front this chamber has a narrow mouth through which the wood can be put into the hearth, which is on the ground. At the top and in the middle of the vault, there is a large round hole which opens to the upper chamber, so that the flames can penetrate into it. Between the arches in the walls of the upper chamber are eight windows, so large that the big-bellied pots may be placed through them on the floor of the chamber, around the large hole. [...]. In the back of the furnace is a rectangular hole [...] through which the heat penetrates into a third furnace which adjoins it.

The third furnace is rectangular [...]; it also consists of two chambers, of which the lower has a mouth in front, so that firewood may be placed on the earth which is on the ground. On each side of this opening in the wall of the lower chamber is a recess for oblong earthenware receptacles [...]. The upper chamber has two holes, one on the right side, the other on the left, of such height and width that earthenware receptacles may be conveniently placed in them. [...] In these receptacles the glass articles are placed so that they may cool in a milder temperature; if they were not cooled slowly they would burst asunder. When the vessels are taken from the upper chamber, they are immediately placed in the receptacles to cool.

Operations were of course more complicated when two furnaces, or only one, were available: from melting and blowing to annealing, a rigorous day/night schedule then had to be followed to optimize furnace use and wood consumption. Furnaces were built with unfired, but dried clay bricks, a highly technical process, but none lasted more than a few weeks before having to be rebuilt. This type of melting furnace would be used with only minor modifications until the seventeenth century [17]. The main

(a)



(b)

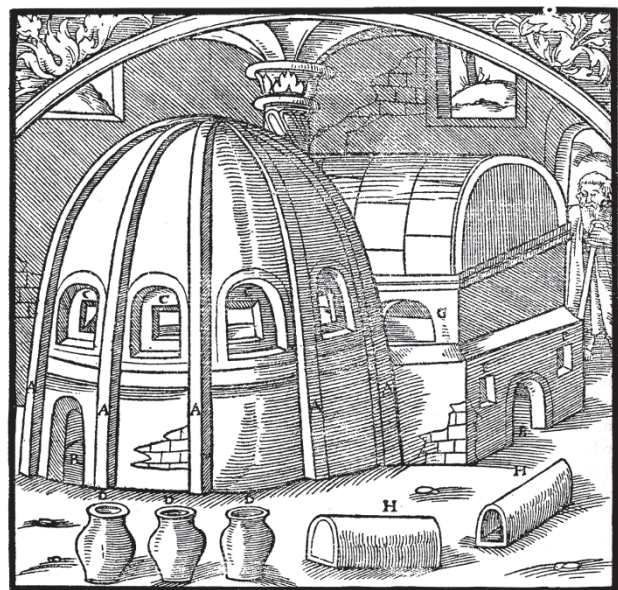


Figure 3 The three glass furnaces described by Agricola [7]. (a) The melting furnace; A: lower chamber; B: upper chamber; C: a vitreous mass. (b) The working and annealing furnaces; A: arches of the working furnace; B: mouth of the lower chamber; C: windows of the upper chamber; D: big-bellied pots; E: mouth of the annealing furnace; F: recesses for the receptacles; G: openings in the upper chamber; H: oblong receptacles.

goal of glassmakers was to increase lifetime through proper choice of clay and design improvement whereas melting temperatures slowly increased thanks to a better knowledge of the heating properties of wood and of ways to improve combustion.

The pots were also made of clay from which heterogeneous parts and fragments of pyrite, limestone, gypsum, or vitrifying matter were carefully removed. Making them required much skill as their breakage and ensuing glass leaks within the furnace was a very serious and costly accident. Of particular importance was the fact that melting had to be carried out in two steps to obtain a glass of satisfactory quality and limit high-temperature corrosion of the melting pots [17]. Under progressively higher temperatures, the first step was aiming at burning charcoal leftovers, eliminating humidity, and other volatile substances, and beginning the decarbonation process to produce a partially melted product named *frit*. The frit, to which the relevant metal oxides were generally added for colored products, was then melted without suffering from settling of the sand in the less dense molten alkali salt that first formed readily. The process would be applied until the nineteenth century to produce containers from very “difficult” types of glasses.

3.2 Reverberatory

The *reverberatory* (from the Latin *re-verberare*, to strike back) furnace (Figure 4) was not a brand new invention when it was first described in Biringuccio’s *Pirotechnia* [6]. Its original feature was to keep the wood fuel and the material to be melted separate. The latter was thus not in contact with the flames or deleterious fumes, but melted instead by the intense heat accumulated and radiated by the vault of the chamber.

Toward the end of the sixteenth century, shortage of wood began to be a serious issue in England where both glass- and steelmakers were badly needing the resource at a time when fierce competition was taking place between glasshouses, fostered by the flight of religious refugees from Northern Europe who had glassmaking expertise [25]. Interest in coal furnaces thus developed rapidly so

that a first patent valid for 21 years was granted in 1610 for the building of coal furnaces for a wide range of products. This goal was too ambitious so that a new patent restricted to glassmaking was granted the following year to a group of investors, who were quickly successful since glass was actually produced in 1612 at Winchester House in Southwark. In the midst of much litigation before the Privy Council, not only were the use of wood furnaces and import of foreign glass prohibited in 1614 but the *Proclamation touching Glass* issued on 23 May 1615 by the king James I (r. 1603–1625) then eventually forbade in England and Wales anyone to “melt, make, or cause to be melted or made, any kind, forme or fashion of Glass or Glasses whatsoever, with Timber of wood.”

The replacement of wood by coal implied important changes on the design of furnaces, however, because deleterious fumes from the smoke colored the glass exposed to the fire and prevented blowers from working before traditional openings. In addition, stronger drafts had to be used to whip up a hotter blaze. In the new furnaces, a long, underground tunnel fed air from outside the glasshouse to the grate at its center. The vault itself was built as a curved *crown* reflecting the heat accumulated from the fire toward the pots that were set around the waist of the furnace on a circular course of brickwork. The pots were covered for protection against soot, smoke, and black drops that fell from the crown. In British window-glass factories, the outer building was frequently of the same shape as the furnace itself, but not in continental glass factories. From this time on, glassmakers sought sites for their furnaces in places where coal was either mined or readily available by boat, which was a major change in their preoccupations. Thanks to the higher temperatures achieved, however, stronger glass could be made, in particular for bottles. But the change from wood to coal took place slowly in France, for example, where only from the

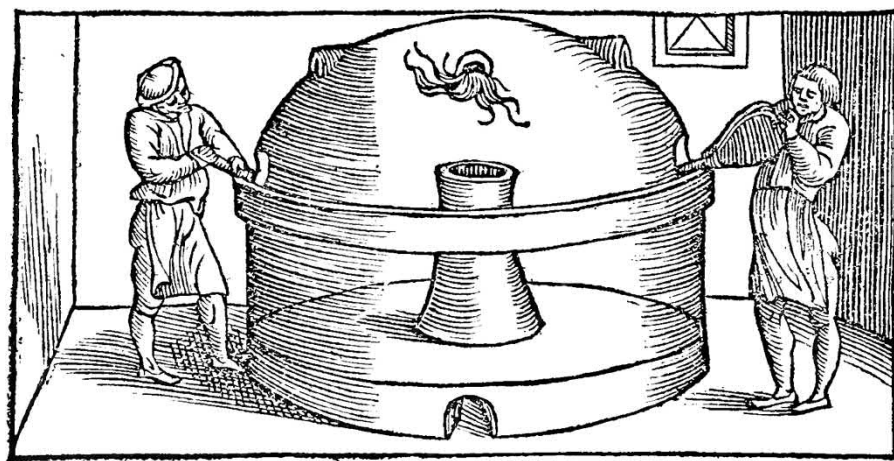


Figure 4 The earliest known representation of a reverberatory furnace in Biringuccio’s *Pirotechnia* [6].

early eighteenth century did bottles become fit to hold effervescent beverages thanks to increases and decreases in the proportions of sand and alkali salts, respectively, made possible by the higher melting temperatures [26].

3.3 Regenerative

As already alluded to, the fundamental advances brought by an understanding of combustion mechanisms and the formulation of the First Law of thermodynamics had important industrial implications when it was understood that heat engines were transforming into useful mechanical work much less than 10% of the energy of combustion of the fuel. An *economizer* was thus early designed by the Scottish clergyman Robert Stirling (1790–1878) for retrieving part of the heat lost to the condenser of his *air engine*. Following in his footsteps, the German-born engineer Carl Wilhelm Siemens (1823–1889), who became known as William, was first involved in 1847 in the design of an engine working with superheated steam whose condenser was supplied with regenerators. The engine was not a complete success so that, with his brother Friedrich (1826–1904) who had come to work with him in England, William turned his attention to simpler problems not involving complex mechanical devices. Such a more readily tractable question was the recovery of part of the energy wasted in industrial furnaces for heating not only the oxygen needed by the combustion reaction but also the nitrogen of the air. The idea was thus to use the huge amount of heat lost up the chimney to preheat these gases to improve energy efficiency. The process was patented in England in 1857 by Frederick for all kinds of industrial furnaces [27]. Its purpose was to let the combustion products

pass over an extended surface of brick, metal, or other suitable material, imparting heat thereto, which heat serves to heat the atmospheric air or other materials of combustion in such manner that the cold air or gases are first brought into contact with the less heated material nearest the chimney, and is brought by degrees into contact with the more intensely heated portions, until it finally passes over that portion of the said surface nearest the place of combustion.

A chamber full of bricks stacked in such a way as to leave as many interstices as possible between them was thus placed between the furnace and the chimney [27]. The burnt gases exchanged their heat with the chamber, cooling down when progressing toward the chimney. After a period of half an hour, for example, the chimney was shut up to let external air enter the hot chamber to be heated up in order to reach the combustion chamber of the

furnace at an already high temperature. At the same time, the exhaust gases were brought into similar chambers for the same period of time before the valves' openings were reversed (Figure 5). Not only was the heat efficiency much enhanced but the higher melting temperatures reached were favorable to the homogeneity of the glass whose quality was thus notably improved. The batch was still melted in clay pots, which were generally smaller at the bottom than at the top to promote regular heat diffusion (Figure 6). Their capacity was typically 400 kg for window and goblet glass in France and Belgium, but of only 75–150 kg in Germany and of up to 2500 kg in England [17].

In contrast to the traditional furnaces, however, the new regenerative ones required very skilled workers to be operated and they much suffered from ash deposition in their checkworks of refractory bricks. The solution found to this serious practical problem was to replace the solid by a gas fuel, which could also be preheated to increase further the heat efficiency. With a first report dating back to the seventeenth century and real industrial production for lighting in the early nineteenth [28], gasification of coal had long been well known when it was then put to use for furnace heating. On 22 January 1861, a new British patent was granted to the Siemens brothers to use a gas mixture of H_2 and CO known as *water gas* prepared in a *gas producer* (Figure 7) by the

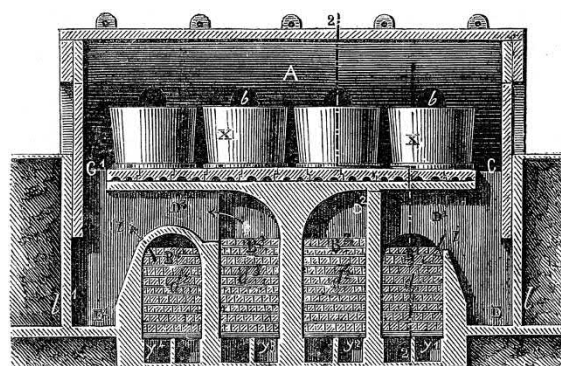


Figure 5 Siemens regenerative pot furnace (width: 6 m): cross section through the furnace (a) and the four regenerators (b) [17]. Open arrays of bricks: d; Pots: X.

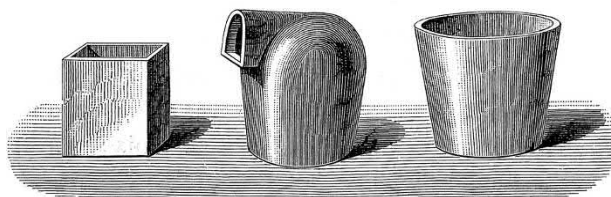


Figure 6 The open and closed clay pots still used in the middle of the nineteenth century [20].

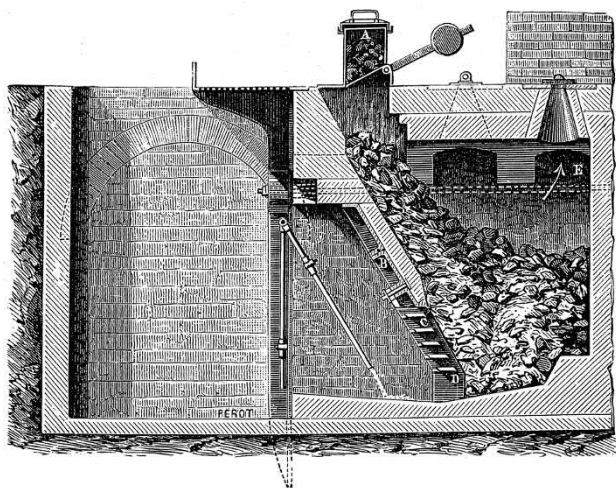


Figure 7 The gas producer of a Siemens regenerative furnace [20]. Coal sliding down the hopper, reacting when red hot with the steam produced by the water coming from the large oblique tube to produce the complex water gas mix exiting toward the furnace in E.

reaction of steam with coke. At the basis of the process was the exothermic reaction



whose efficiency was improved if steam was blown onto the red-hot coal to produce hydrogen according to:



The water gas produced was actually a complex gaseous mixture in which, not surprisingly, nitrogen was predominating. Compositions of 24.2 vol % CO, 8.2% H₂, 2.2% CH₄, 4.2% CO₂, and 61.2% N₂ were, for instance, later reported at Saint-Gobain [29].

In addition to fuel savings up to 50%, advantages were the possibility of using lower-quality coal, a greatly increased operational facility, a more complete combustion reaction, and, thus, an almost lack of smoke, which was another important asset for making glasses of specially high quality, for example, for optical lighthouse lenses. In England, the first regenerative glass furnaces were built in Rotherham and Birmingham. The advantages of these new furnaces were such that many were already in use, in construction or ordered in Europe only two years later [30]. They included now four at Chance Brothers and Co in Birmingham (more being built), two in Dresden for Siemens and Mehlis, one in Glasgow for Stevenson & Co, two near Hamburg for Broederson & Co for sheet and container glass, two in Montluçon glass-works (central France), five at Saint-Gobain (five more ordered), and two for the British Plate Glass works, near St Helens in England, for plate glass and several for crystal glass or metallurgy.

As an example, the new 16-pot gas-regenerative furnace built by Saint-Gobain in its Glacerie of Cirey in 1864 produced 5793 m² of plate glass in 33 castings and consumed only 48 kg of coal per square meter of plate glass, representing a 50% savings on fuel consumption [29]. Initially, many features of traditional furnaces were of course retained. The burners were, for instance, set in the sieve where the pots were lying and where the grates separating the chamber from the hearth were previously placed so that air and the combustion gas were still admitted vertically. Progressively, further modifications were thus made to increase heating homogeneity via changes in the geometry and distribution of the burners so that batches were melted at the same rate in all pots. As cooled from the bottom by air circulation, furnaces had a lifetime of 16–18 months.

3.4 Radiative

In all types of furnaces hitherto designed, it had been considered that bringing the flame in very close contact with the batch was necessary to achieve efficient melting. Back in Germany in 1864 to take over a family glasshouse in Dresden after the death of another of his brothers, Friedrich Siemens thus signaled an important conceptual change when, reflecting on the nature of heat, he concluded that “combustion can only be perfect, and be maintained perfect, if the space in which it takes place is sufficiently large to allow the gases to combine out of contact with solid materials.” This condition implied that the “flame must not be allowed to impinge upon bodies to be heated, but must simply heat the bodies by radiation, and furnaces must be so constructed as to allow to the flame out of contact, not only with the substance on its bed, but with the walls and roof of the furnace itself” [31].

In these large furnaces, one reduced the production of soot by contact of the flame with colder surfaces by placing the gas and air inlets at a small distance of the crown of the heating chamber, and also of its walls, so as to leave a large space available for burning and flame development. Enough space had also to be left between the pots to ensure an even radiative heating. Large fuel savings could be made in this way, indirect additional advantages being in many cases an increased yield, higher glass quality, and an extended lifetime for the pots. These innovations would in fact pave the way to the tank furnace. Other configurations were nonetheless experimented. The gas-producing unit was, for example, installed close to the furnace itself and the regenerator used only for the air, the gas being directly injected into the furnace without being heated. The new furnace was much smaller, usually half the previous one, and thus cheaper to build but was operating with only 25–30% fuel savings (Figure 8).

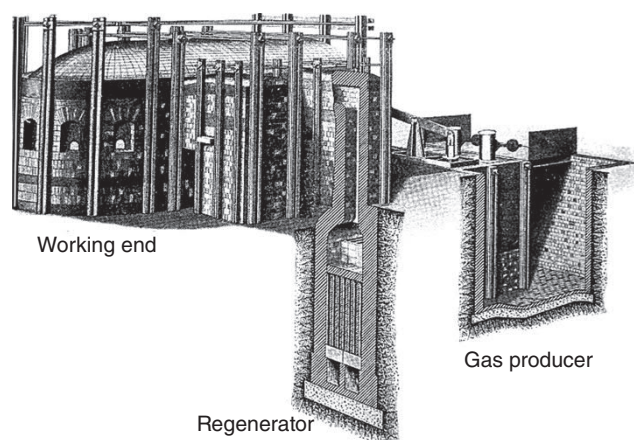


Figure 8 The mutual disposition of Siemens furnace, gas producer, and regenerator [32].

In 1893, a comparison made between the traditional furnaces with burners in the sieve and the new ones with burners in the wall showed that the glass was of a much better quality when melted in radiation pot furnaces, but also that the crown was attacked because its height was too low [33]. Following furnace modifications at Saint-Gobain, it was concluded three years later that burners were more advantageous when placed in walls even though their fuel consumption was not lower [33]. After a slow start, these burners made operating conditions more regular because of the large amounts of heat stored in the refractory materials. In addition, they were easily accessible and easier to maintain; the crown was less attacked and the regenerative chambers were more durable thanks to decreased deposits; as for the pots, they were less violently attacked and, thus, more uniformly heated. True, the older furnaces could also ensure good glass quality but only for the initial periods during which combustion was optimal, which did not last long.

3.5 A Revolution: The Regenerative Tank Furnaces

When designing the tank furnace, engineers did not know that they were not breaking completely new ground, but rather much improving a concept already adumbrated in antiquity (Chapter 10.3). Originally, the Siemens brothers were not yet sure whether they might use real *tanks* without pots, but they readily solved the various problems caused by inadequate refractory blocks. Pots did vanish from the scene (Figure 9). In a design patented in 1872 [35], the tank was partitioned in three compartments

arranged to communicate with each other in a manner that the raw material is introduced and melted down in the one compartment, from the

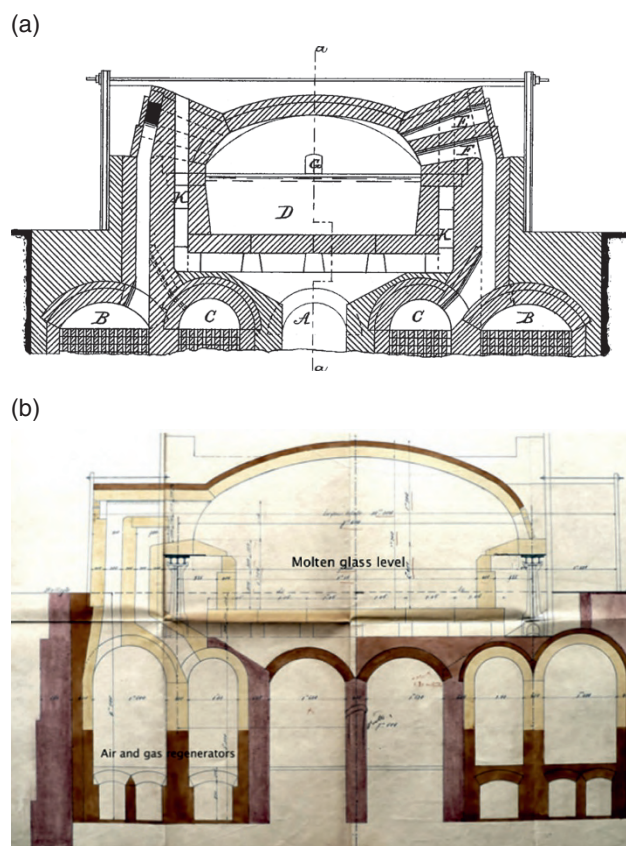


Figure 9 From blueprint to actual construction, the new tank furnace with a deep melting area. (a) Siemens patent [34]; A: cave with the regenerative chambers B for air and C for gas; D: tank 18 in. in depth; E and F: “flues conveying the heated air and gas up from the regenerating chambers on one side, while the products of combustion pass down by corresponding flues to regenerative chambers on the other side” in a movement alternated from time to time. (b) Saint-Gobain furnace built in 1890. Source: Courtesy archives Saint-Gobain.

lower part of which the melted material is caused to flow into the top of the next compartment, whence it passes into the bottom of the third compartment, from which it is worked out.

As summarized in a subsequent patent [34], “no time was lost in cooling and settling the metal and reheating the furnace,” whereas “the tank was rendered more durable by being subjected to a uniform temperature and an economy in labor was effected in lessening the number of workmen required for the melting operations.”

The beginnings of the new furnace were not necessarily trouble free, however, as experienced in 1872 by Pilkington Brothers whose first tank failed suddenly after a promising one-week operation because worn-out bottom refractories caused the whole furnace to collapse. Design improvements first allowed a second tank to run nonstop

for 97 days and then led pot-furnaces to be abandoned at a rapid rate as 12 tanks were working in May 1877 and more were being built. At that time, tanks were 9 ft wide and 36 ft long. When new, they held 2 ft 6 in. of melted glass and then smaller amounts when the side refractories were wearing thin and thus becoming subject to bursting. As a matter of fact, the rapid wear of refractories required their renewal every 3–4 and 10–11 months for the sides and bottom of a furnace, respectively. In both cases, the operation took about three weeks. One more improvement was then brought when the depth of the tanks was increased (Figure 9) to form “a layer of chilled glass on the surface of the bottom, at which point the movement of the particles cease, whereby the bottom blocks will be protected from wear, the presence of stones in the glass avoided, and a larger proportion of high-quality glass will be produced” thanks to the fact that “the tank is maintained full of metal” [36].

3.6 Toward Continuous Processes

As summarized by M. Cable [37], “the regenerative tank furnace was the greatest advance in glass technology since Roman times.” The raw materials were fed at one end to be melted when progressing toward the other end where the *metal* was cooled down to reach the right viscosity for the shaping operations. Window glass manufacturing thus became close to be a nearly continuous process. The glass no longer needed to be melted for 24 hours in pots, which ensured the aforementioned time, fuel, and labor savings. Sheet and container glass-makers were among the first to adopt the new regenerative tank furnace in Britain and continental Europe, but less so in the United States, where the first was not built until 1889.

At the Compagnie de Saint-Gobain, however, the new technology was not regarded as capable of producing good-quality plate glass. The first tank furnaces were eventually built to produce rolled glass in the Saint-Gobain plant in 1881 and two in Stolberg, the first in 1884 and the second, an end-fired furnace, in 1888. Valuable data on the yield of these tank furnaces are found in a 1911 internal report where a plant manager recorded productions of 0.48, 0.4, and 0.36 tons per day and m² in Montluçon, Saint-Gobain, and Pisa (Italy), respectively, which are actually only a few times lower than achieved today in float-glass plants (Chapter 1.4).

The crown process had been abandoned since the end of the previous century. It could no longer compete with the cylinder process because of its smaller, circular sheets, less uniform thickness, and much higher waste upon cutting. But the increased throughput ensured by tank melting required more efficient methods for flattening the cylinders and annealing the flat glass obtained

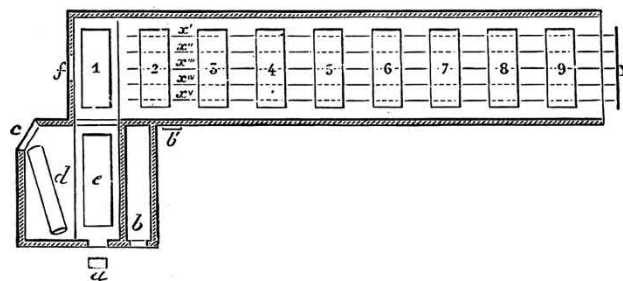


Figure 10 Bievez lehr for the annealing of nine glass sheets [38]. Newly made sheet introduced in e; hearths in b and b'; sheets lying on iron frames moved to the next place from one to nine by a set of iron bars raised by a lever placed in Y.

[10]. In the new type of annealing *lehr* (*pattern*, in German) patented in 1866 by the Belgian worker Désiré Bievez [38], a much improved productivity resulted from movable tables carrying the sheets to be cooled, which entered at right angles from the flattening furnace (Figure 10). These were laid upon frames furnished with counterbalance-weights to facilitate their upward and downward motions given by a lever placed at the end of a connecting-bar. Moving all the sheets successively from first to last place was so easy that two annealing furnaces could be operated at the same time by a single worker. The new process ensured not only a reduction of the annealing time from 7 to 8 hours to 25–30 minutes, but also a better flatness and improved mechanical properties thanks to the same cooling rate applied on both sides of the sheets.

3.7 Rolled, Printed, and Wired Glass

Thanks to its perfect match with glass, the steel introduced in a highly visible way in the early nineteenth-century architecture enhanced the demand for large glass panes. As a consequence, processes were improved to make panes wider and at lower cost. In the rolled-glass process [39], the melt was ladled directly from the melting pot onto the casting table and rolled as done for plate glass. One, two, or more ladles could be used for one sheet, which could thus be made long and narrow and also thinner than usual plate glass at a cost much lower than with the cylinder process. Weight and cost advantages led this glass to be extensively used for greenhouses or roofs of railway stations. Well-known examples were in London the Crystal Palace (Figure 11) and the Paddington Great Western Railway Station (1858), in Paris the greenhouses of the Jardin des Plantes (1854) and the former Halles centrales (1855), or in Milan the Prato Centrale railway station (1862). The annual production thus rose to more than $0.56 \cdot 10^6$ m² in 1884 and reached $0.92 \cdot 10^6$ m² in 1898.

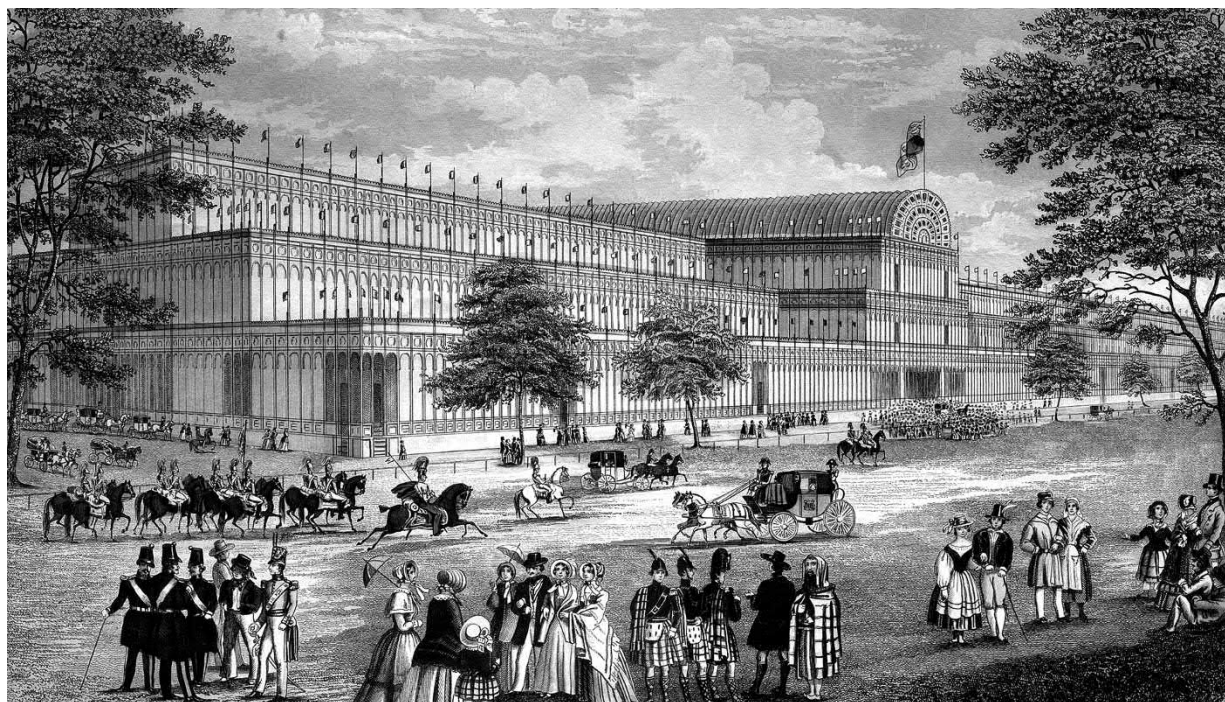


Figure 11 The original 563 × 139 m large and 39 m high Crystal Palace designed in two weeks by the famous gardener Joseph Paxton (1803–1865) and built on time and on low budget in Hyde Park in London for the 1851 Grand International Exhibition. Its shape and size were entirely scaled from the maximum 10 × 49 in. size of the flat-glass panes produced at that time by Chance Brothers under the direction of G. Bontemps; French workers had to be brought to help produce the total of 84 000 m² of glass that were displayed in just five months within a 4000-ton iron framework. After the six-month Exhibition, the Palace was dismantled and re-erected enlarged at the top of Sydenham Hill where it was destroyed by a blaze in 1936.

Compared with plate glass, these sheets were of a lesser quality but their lower prices made not only new applications but also new processes possible. A case in point was the machine successfully developed in 1884 by George and Edward Chance, whereby the molten glass was poured down an inclined plane to pass in between a pair of iron rollers [40]. In 1890, the process was improved with the addition of a second pair of rollers to impress a given pattern. Printed glass was born.

Following this invention, another machine was developed in Paris by Léon Appert (1837–1925) to make wired glass. His first wiring machine combined two rollers in between which glass was poured in two successive layers to embed the wire. Later on, the process was simplified: the wire was clamped above the table at the correct height and the glass cast and rolled in the usual way. The roller forced the fluid glass through the meshes of the wire, to unit again beneath it, thus giving the desired result in one simple operation (Figure 12). Interestingly, from 1879, Appert had also been a pioneer in the use of compressed air to blow glass faster, bigger, and with a much improved hygiene because workers used to share their blowing pipes [41].

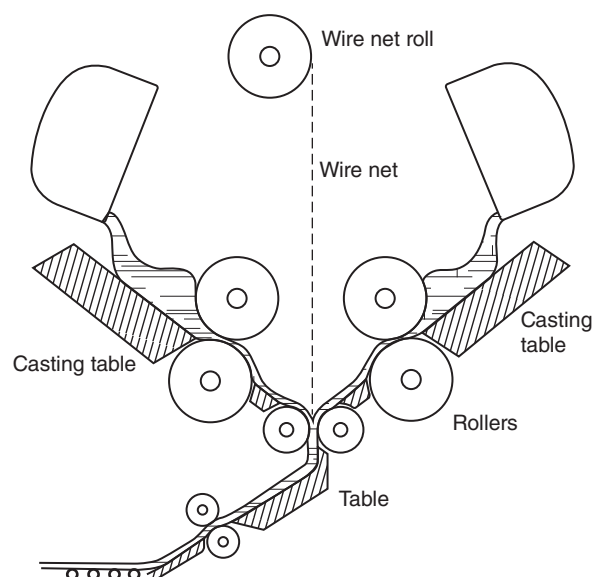


Figure 12 The making of wired glass from glass cast on two converging tables.

4 Plate Glass

4.1 Mirrors: From World-Famous Venice to Newborn Saint-Gobain

It was only with the advent of the float process in the 1960s (Chapter 1.4) that the age-old distinction between sheet and plate glass was abolished when surface smoothing became superfluous for the latter. Traditionally, glass had been produced thicker for plate than for window glass to bear first grinding with sand and then polishing with *rouge* (red, iron oxide) in order to impart the desired lustrous finish to its surface. While window glass was becoming common in the seventeenth and the eighteenth centuries, plate glass remained a luxury product. Because of its thickness, any discoloration was clearly noticeable whereas defects within the glass itself or surface unevenness meant that the product would fetch much lower prices.

The emphasis, therefore, had always been put upon high quality, which was the problem already solved by the Venetian glassmakers through the preparation of the raw materials and the control of the melting conditions of their *cristallo* glassware (Chapter 10.7). Only the purest ingredients thus went into the manufacture of this glass, namely the best alkali salts and pure silica in the form of expensively ground quartz pebbles. The whole batch was then very carefully prepared and fritted before being introduced into the melting pots. The fame acquired by Venice through the *cristallo* of course motivated foreign competitors to imitate its production in the form of glass pieces *à la façon de Venise* (in the fashion of Venice), which could be hardly distinguishable from the genuine production. As complained around 1607 by a glass dealer in Antwerp, “one counterfeits Venetian glasses so well that glass makers themselves are able to discern the difference only with great difficulty” [26].

The fame of Venetian glass was due not only to the *cristallo*, but also to the quality of the mirrors sought after by the wealthy Europeans. Thanks to their fire polish, the best were the curved mirrors known as *œil de sorcière* (sorcerer’s eye), which were directly cut from blown ware but were necessarily small. The importance of the market for larger mirrors represented a real incentive to newcomers so that the French king Louis the 13th published in 1634 an edict allowing two supposedly successful makers “to establish in this city of Paris a manufacture making plate glass for mirrors with special prerogative for a few years” [29]. Despite the hiring of workers from Venice and Altare, however, no progress was actually made so that a *Manufacture Royale des Glaces* was created in 1665 by Colbert (1619–1683), the French minister of finance. Even though it was privately owned, the new

company benefited from impressive financial and honorific privileges such as the royal coat of arms affixed on its gate or the livery that the gatekeeper was allowed to wear. In 1672, Colbert could eventually tell Louis the 14th that “our mirrors are now more perfect than those of Venice” [29] as actually illustrated by those of the famous *Galerie des Glaces* in Versailles. These had been produced in 1685 from cylinders made at Tournlaville (near Cherbourg, in Normandy) and silvered in Paris, close to the market to prevent such a valuable product from being broken upon long-distance transportation.

But the cylinder method had serious disadvantages. Sizes could not be greater than about 1 m (in modern units) because cylinders blown longer would have become too thin to be ground. The solution was thus to improve the old Roman casting of glass onto a very flat table. The inventor of the process was probably an elusive Bernard Perrot from Orléans [42]. Better known is the fact that a group of businessmen were granted Letters Patent in 1688 that gave them a monopoly for the manufacture of the cast plate glass for the French market and, later, for export as well. The new *Société des Grandes Glaces* rapidly moved its factory to the village of Saint-Gobain in Northern France where wood was cheap and plentiful. After eventful early years during which bankruptcy was lurking, the company eventually met with success and threatened the existence of the *Manufacture Royale* because of the much larger size of its own glass plates. In the end, Louis the 14th decided in 1695 to merge the two companies into the *Manufacture des Glaces de France*, which would become much later the *Compagnie de Saint-Gobain*.

To produce plates as large as about 3×2 m, the two major improvements of the new process were a large iron table used for casting and a heavy iron roller driven by two workers to flatten the glass into a sheet once any visible defect had been hand-removed (Figure 13). Two iron slips along the edges of the table determined the thickness of the plate whereas two other cast-iron guides fixed its width and prevented the glass from flowing onto the side-slips. After glass casting and hardening, the table was moved toward special kilns (*carcaises*) where the plate was cooled down and annealed before being ground, smoothed, and finally polished. The first two of the last operations were similar in that they consisted in smoothing the surface of the glass with a sand abrasive applied with iron plates. Upon grinding, most of the excess glass was removed with coarse sand before the defects introduced along the way by the bigger grains were eliminated with a finer sand. The glass surface then had a dull, gray appearance so that a polished surface was obtained through rubbing with iron oxide (*rouge*) applied with a felt-covered tool.

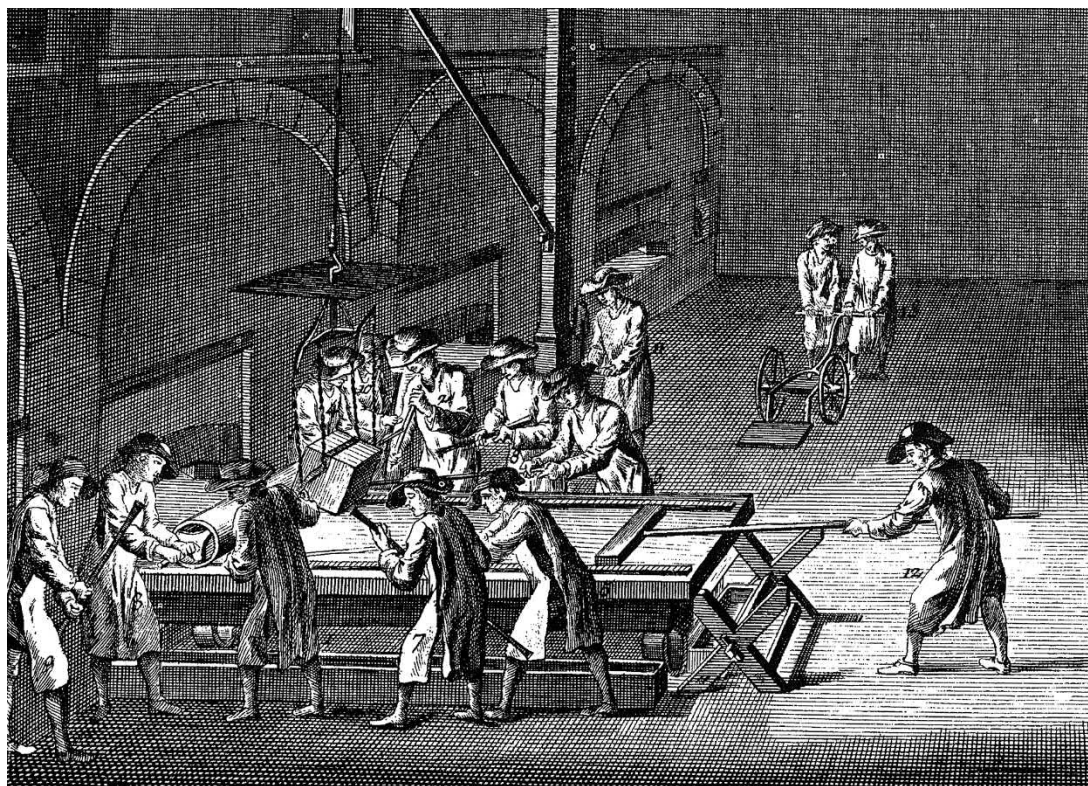


Figure 13 The original Saint-Gobain casting process for plate glass: glass poured from the pot brought by the crane and spread with an iron roll before being transferred for annealing to a one of the horizontal *carcaises* on the left-hand side in the background [16].

4.2 A Craving for Plate Glass

In theory, the casting process was straightforward. In practice, however, it required not only much manpower but also a very large capital outlay as three million pounds were, for instance, spent between 1665 and 1702 by the French investors [42]. Instead of the small customary glasshouse, a wide hall was needed with a large melting furnace in the center, a casting table, a crane to transfer the pots from the furnace, a series of *carcaises* for annealing each plate made at a time, the machinery required for grinding and polishing [8], and also a storage warehouse. Such large investment cost makes it understandable that Saint-Gobain did not have many competitors for a long time, in England from only 1770 when former Saint-Gobain employees were hired at Ravenhead without having really been able to match the original quality [42]. The advantages of the new plates were such, however, that architects installed large mirrors in the halls, galleries, and reception rooms of the very affluent to play with light and shadow and create intriguing perspectives. Market demand thus increased smoothly but steadily through the eighteenth and nineteenth centuries when applications included not only large mirrors fixed above fireplaces and other elements of architectural decoration in

bourgeois apartments but also shop windows, making at the same time larger sizes desirable (Table 1).

Melting kept being made in pots containing about 2.5 tons of glass in regenerative gas furnaces, preceding casting and then annealing in *carcaises*. In 1893, $2.4 \cdot 10^6 \text{ m}^2$ of plate glass were manufactured in Europe at a cost of 15 francs per m^2 in France, which was down from 95 F in the 1820s thanks to cheaper soda (Chapter 10.11) and continuous increases of the size and efficiency of the furnaces [42]. In 1897, seven plate-glass factories were in operation in France, five in Belgium, six in Germany, six in England, one in Russia, one in Italy, and four in the United States. The surface produced in Europe had then increased to $3.6 \cdot 10^6 \text{ m}^2$. During this period, the US production increased from $0.5 \cdot 10^6 \text{ m}^2$ in six factories to $1.2 \cdot 10^6 \text{ m}^2$ in 13. In parallel, the time needed to make plate glass had been halved since 1765 thanks to the introduction of new mechanical means for casting, grinding, and polishing [29]. This importance of machines in glass-making was acknowledged by the high hierarchical levels reached in glass companies by mechanical engineers, as illustrated by Lucien Delloye (1856–1938) who ended up being the very influential head of the plate-glass division of Saint-Gobain [43].

Table 1 Maximum size and price of plate-glass sheets [33].

Date	Surface area (m ²)	Length (m)	Width (m)	Price for 1 m ² (1 × 1) in French francs
1806	4.25	2.50	1.70	226 (1805)
1839	8.73	3.80	2.30	127 (1835)
1844	11.66	4.30	2.70	
1855	18.40	5.40	3.40	61 (1856)
1867	21.80	5.90	3.70	47.75 (1862)
1878	26.50	6.40	4.10	40.30 (1884)

4.3 Toward Continuous Processes: Bicheroux and Boudin

The move from batch to continuous production of plate glass eventually began between 1910 and 1914 with the process designed by the Belgian engineer Max Bicheroux in Herzogenrath (Germany), a factory owned at 50% by Saint-Gobain from 1905. As somehow derived from the Chance process, the new one [44] consisted in casting the glass melted in pots between two iron rollers on a table whose tilt was increased as casting proceeded and the glass was cooling (Figure 14). But the period of the First World War was of course not the best to promote technical innovation in glassmaking. Whereas most plate-glass factories were still using late nineteenth-century methods in 1919 [29], Bicheroux’s innovation did spread in the 1920s in most plate-glass works not only at Saint-Gobain but also in other companies after a license had been sold to all European and American plate-glassmakers within the framework of the 1904 *Convention Internationale des Glaceries (Plate-Glass International Convention)* founded at the initiative of L. Delloye.

Another innovation was the tunnel furnace designed to anneal plates slowly moving in a temperature gradient from 650 to 550 °C in about half an hour. Thenceforth, casting tables of 10 × 5 m had no longer to be moved from the casting spot to the carcase but could be fixed and reinforced instead, which was much more favorable for product quality. At the same time, better use was made of mechanical power for the grinding and polishing process.

To get closer to a continuous process, the obvious next step was to substitute tanks for pots for glass melting. It was the development of alumina-based electro-cast refractories in 1925–1930 that made this substitution possible. After it had been noticed that some *stones* were so difficult to dissolve that they might yield better refractories if they could be melted, these materials were first synthesized from sillimanite (Al₂SiO₅) at Corning Glass Works in 1923 by H.P. Hood and G.S. Fulcher (1888–1871), of VFT viscosity-equation fame (cf. Chapter 10.11), for providing a better resistance to glass

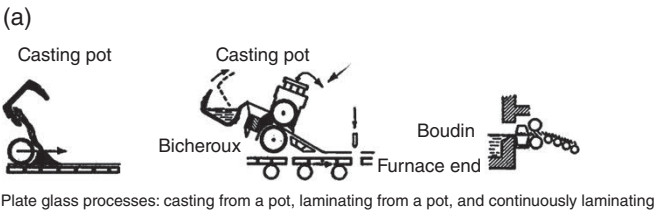


Figure 14 Plate glass processes. (a) Sketch of the evolution. (b) Glass flowing from the melting pot in the Bicheroux process at the Herzogenrath plant in 1966. Source: Photo courtesy Saint-Gobain Archives.

corrosion. After melting with the electric-arc, these liquid oxides indeed crystallized as dense refractories with a low porosity that reacted much less with the molten glass than previously available materials. The new refractory

was made by Corning not only in the United States in 1927 for its expanding lighting glass-bulb business in a joint venture with Hartford Empire (Chapter 6.9), but also in France in 1929 and Japan the following year through other joint ventures with Saint-Gobain (which has become the current SEPR company) and Asahi Glass Co. [45]. Use of the new refractories for melting tanks was then rapidly implemented by Louis Boudin (1875–1967) in 1932 in the then most recent Saint-Gobain plate-glass factory of Chantereine, north of Paris. Even though the still hot glass tended to subside between the two rollers, the continuous sheet obtained was at least as good as that obtained by the Bicheroux process (Figure 15). By the way, this is the reason why the Boudin process is still used at present to manufacture printed glass.

4.4 Short-Lived Mechanical Feats: Continuous Grinding and Polishing

It still remained to grind and polish the plate glass on line to arrive at a fully continuous process. The initial impulse in that direction was given by a strong need for



Figure 15 The 3.2 m large continuous glass ribbon exiting the annealing lehr to be continuously ground and then polished with the Jusant machine, Chantereine plant, Saint-Gobain. Source: Photo courtesy Saint-Gobain Archives.

windshields when car production began to increase very strongly in the United States in the 1920s [24]. Without any experience in glassmaking, the Ford company was able to design a machine casting a ribbon large enough to make 40 in. windshields but it could not produce a glass of the required quality in a tank furnace. Through collaboration with Pilkington Brothers, the whole process was improved not only for melting but also for grinding of the glass pieces, cut right after annealing, in two distinct steps for the upper and lower side.

Additional developments were then made by Pilkington for the general production of plate glass in the form of a 60 in.-wide ribbon in 1924, and then of 100 in. in 1927, which could be ground continuously [24]. What was further needed was a machine that could grind and polish the glass ribbon on both sides as it emerged from the lehr before being cut into plates. Only the first operation was made with the twin-grinding process developed by Pilkington, however, which came into service in 1935. The twin grinder first ran at a speed of 1 m per minute, which was later increased by a factor of 5. It came to be used by all the main manufacturers in the world for the greater part of their plate glass production. But polishing was still made side by side on the sheets cut out of the glass ribbon whereas a glass fraction of about 30 % was lost in the grinding and polishing operations.

After having bought a Pilkington license for the twin grinder, Saint-Gobain went one step further with a complex polishing machine, the Jusant, whose prototype was installed in Pisa in 1956 to polish after grinding the glass ribbon emerging from the annealing lehr in a continuous way. Full production then began in November 1959, with a bigger machine installed at the Chantereine plant (Figure 16). The new process represented a mechanical feat, which was the culmination of an evolution that had begun three centuries earlier. But it was very costly in terms of both investment and operation, with 110 workers on the line, and kept wasting about 20% of the glass that was mixed with the abrasive products. Hence, it came too late and could not compete with the float process, which began production in the very same year (Chapter 1.4). The Jusant was thus discontinued after 10 years of use even though it was certainly producing the finest plate glass ever made at a rate of 15 000 m²/day.

5 Container Glass

5.1 The First Machines: Ashley and Boucher

By making continuous production possible, the Siemens tank furnace ensured a much greater output than the old pot furnaces as well as lower fabrication costs. For bottle production, working holes were opened in the melting tank just above the glass level in front of which fireclay



Figure 16 Aerial view of the Jusant polishing machine. Total length of the line: 420 m. Polishing made with an aqueous suspension of Fe_2O_3 and FeSO_4 powders at an applied pressure of 50 kg/dm^2 exerted by nine machines, each made up to two pairs of two drums rotating at 600 rpm according to an eccentric circular motion in opposite directions above and below the glass ribbon. *Source:* Photo courtesy Saint-Gobain Archives.

rings were floating to allow a clean glass without scum or stones to be gathered for blowing made in the traditional manner. In 1886, Howard Ashley, of Castleford in England, reflected that much of the preliminary work to shape parisons (gobs) for mold-blown bottles might be performed mechanically. He introduced the parison or initial shaping mold, equivalent to the preliminary marvering and blowing of the glass. A further improvement by the same inventor was the use of compressed air for blowing up the bottle in the finishing or *blow* mold.

In France, the self-taught Claude Boucher (1842–1913) had been a pioneer when he built in 1878 a melting tank for the bottle-glass workshop he founded in Cognac. Later on, he designed in 1894 a manual compressed-air machine to replace the glassblower in all operations except gob gathering in the furnace [46]. The first mechanical bottles were made and sold in 1898. It then

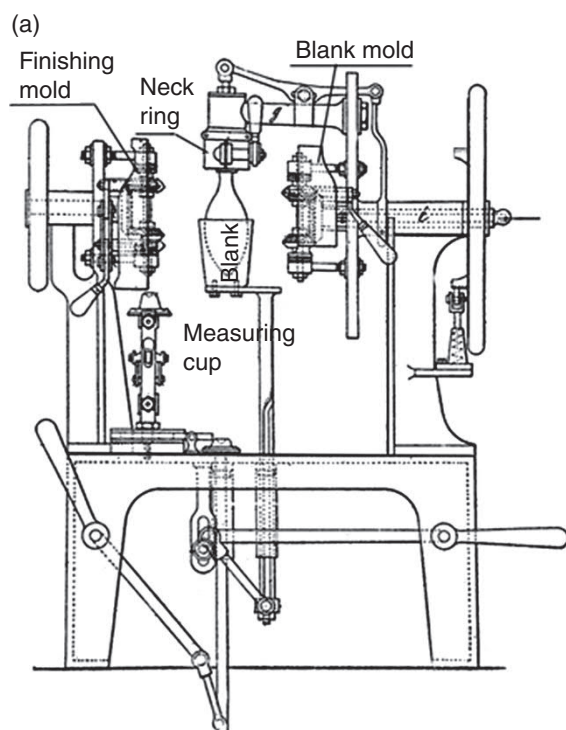
appeared that its use allowed workers to be trained in a few months instead of 10 years and bottles to be produced 2.5 times faster (i.e. 120 per hour) and even 25 % faster than with the Ashley machine thanks to two alternating parison molds: while one was filled, the other could be used to shape the parison; as soon as the parison was blown and transferred to the finishing mold, the system was reversed to blow the glass already injected in the first mold (Figure 17). In 1906, 108 of his machines were working in many factories in France alone.

5.2 Finishing First

The late nineteenth-century pioneers had recognized that the finish of the container should be the first and not the last step [47], and that much of the work of a skilled blower's dexterous hand could be replaced with simple operations involving one mold to form the parison and another to blow the container itself. But their machines were still relying on a manual gathering step so that it remained to devise an automatic machine that would supply gobs of uniform weight and temperature. This problem thus slowed down complete automation of the process. It was not really solved until the early twentieth century, but then the new processes did not spread before the end of the First World War. So many qualified workers had disappeared that it is this labor shortage that induced glassmakers to use completely automated processes as the only possible way to supply the existing demand.

Physical properties such as density, thermal conductivity, viscosity, and surface tension and their respective relations to temperature all entered the problem [48]. Any changes in these parameters were at once noticed by a skilled worker who could address them through suitable and sometimes subtle adjustments of the duration of the gathering, marvering, and blowing operations or of the time of contact between the glass and the mold. Since a mechanical substitute could of course not compete in these respects, inventors had to find ways to ensure the constancy of the relevant parameters. They did it slowly and laboriously.

One of the first problems to be solved was that raised by the chemical composition of the glass. As late as in the early nineteenth century, these compositions were themselves problematic as they could devitrify readily because the emphasis was put on the low cost of the raw materials. English bottles of the late sixteenth and early seventeenth centuries could, for example, had less than 6 wt % Na_2O + K_2O but up to 40% CaO + MgO with liquidus temperatures higher than 1200°C , which could thus be managed in the furnaces of the period [49]. Even before the introduction of semiautomated machines, the ratio between alkaline earth and alkali oxides had already been reduced so that by 1904 they became compatible with modern



(b)



Figure 17 Boucher machine for making bottle-glass. (a) The first version. (b) Operation of the machines after manual gathering of the glass through the series of openings in the tank furnace. Oil painting (73 × 116 cm) of the workshop founded in Cognac by Boucher (standing on the left) made in 1904 by René Hérissou (1857–1940). Source: Photo courtesy Musée des Arts de Cognac.

processes [50]. In the end, bottle glass progressively had become the soda-lime silica long used in tableware and flat-glass productions. Along with decreases of Al_2O_3 from 6 to 1% and of CaO from 20 to 7%, continuous increases of Na_2O from about 6 to 18 wt % and of SiO_2 from 60 to more than 70 % have, for instance, been well documented for English bottles throughout the nineteenth century [51].

5.3 The Feeding Problem

Not surprisingly, the first machines attempted at duplicating the gatherer's movements [48], but such *punty feeders* did not prove successful in this respect. Letting the glass flow by gravity from a hole in the glass tank was thus an obvious alternate option that was implemented in different ways in actual industrial production. The Homer Brooke feeder (Figure 18) is the best known of this type: a continuous stream of molten glass issued from the orifice fell onto a table supporting the parison molds. The device consisted of a series of cup-shaped cutting members and corresponding shear blades, which rotated in opposite directions about a central vertical shaft. A stream of glass flowed from the tank into one of a series of receptacles or molds, which rotated step by step about the central shaft. The opposite rotation of the cups and the shear blades caused them to meet and sever the stream before the cup was raised to support the stream while the mold was replaced by another. The cup then turned over and delivered its glass into the mold now

in place. But the device was actually so complicated to use that it had difficulties to compete with hand-gathering!

5.4 The Suction Feeder and the Owens Machine

At about the same time a completely different process relying on the principle of *suction* was successfully developed in the United States by Michael J. Owens (1859–1923). His machine [47] was operated next to an auxiliary furnace and included a revolving pot with a combustion chamber 3 m in diameter and 20 cm in depth, which was continuously supplied from the tank (Figure 19). A portion of the revolving pot projected somehow beyond the walls of the combustion chamber, exposing a segment of the glass surface. The gathering molds of the machine dipped into this exposed molten glass consecutively as the machine rotated; when dipped into the glass, a mold was automatically sucking it otherwise a vacuum would have been created within it, thereby forming the parison. As the mold rose up and moved away from the glass, a knife automatically cut off the string of glass that remained attached, dropping that portion back into the furnace. After the formation of the parison by partial blowing, the remaining steps of the process were similar to those of other types of forming machines, except that no inversion of the blank was necessary before the blowing step. The blank was simply transferred from its mold to the blowing mold suspended by the neck-ring mold.

In 1916, labor represented 53, 48, and 25% of the production cost of a bottle in handmade, semiautomatic, and Owens automatic processes, respectively [52]. Once the capital for the tank furnace, rotating pot and machines had been raised, the economic advantages of the Owens machines became obvious, but only after a while (Tables 2 and 3). Initially, it was not so much lower production costs that were advantageous, but rather the highly standardized and well-finished aspect of the bottles [53]. As one of the first automated machines, Owens' was quite successful in the United States but not in France where the investment problem raised, for example, by the high cost of molds was compounded by technical difficulties. In spite of furnace rotation, the quality of the glass was somewhat degraded by the periodic suction step. Even though automated machines could widely increase productivity, bottle makers generally preferred to keep their Boucher machines while waiting for the likely development of a successful gravity feeder.

In addition, the Owens machine did suffer from one technical defect that never got fixed [47], namely the formation of a "cut-off scar" at the bottom of the bottle where the tail that formed while the gathering mold lifted from the rotating pot was cut and chilled by the knife. As

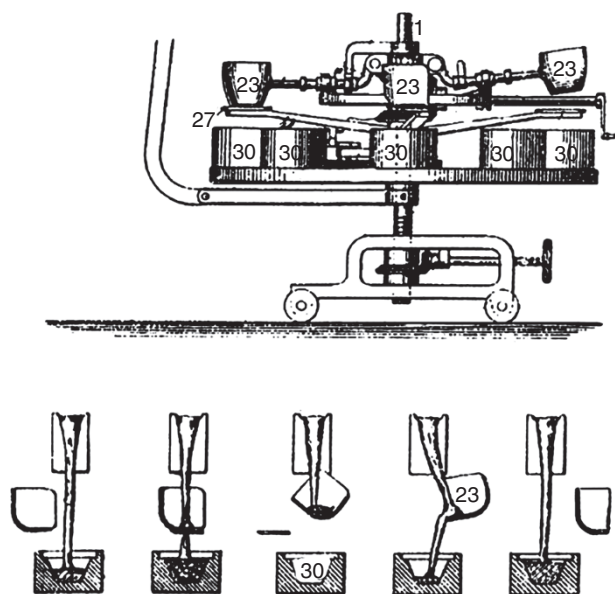


Figure 18 The Homer-Brooke feeder; 1: central vertical shaft; 23: cup-shaped cutting members; 27: shear blades; 30: molds.

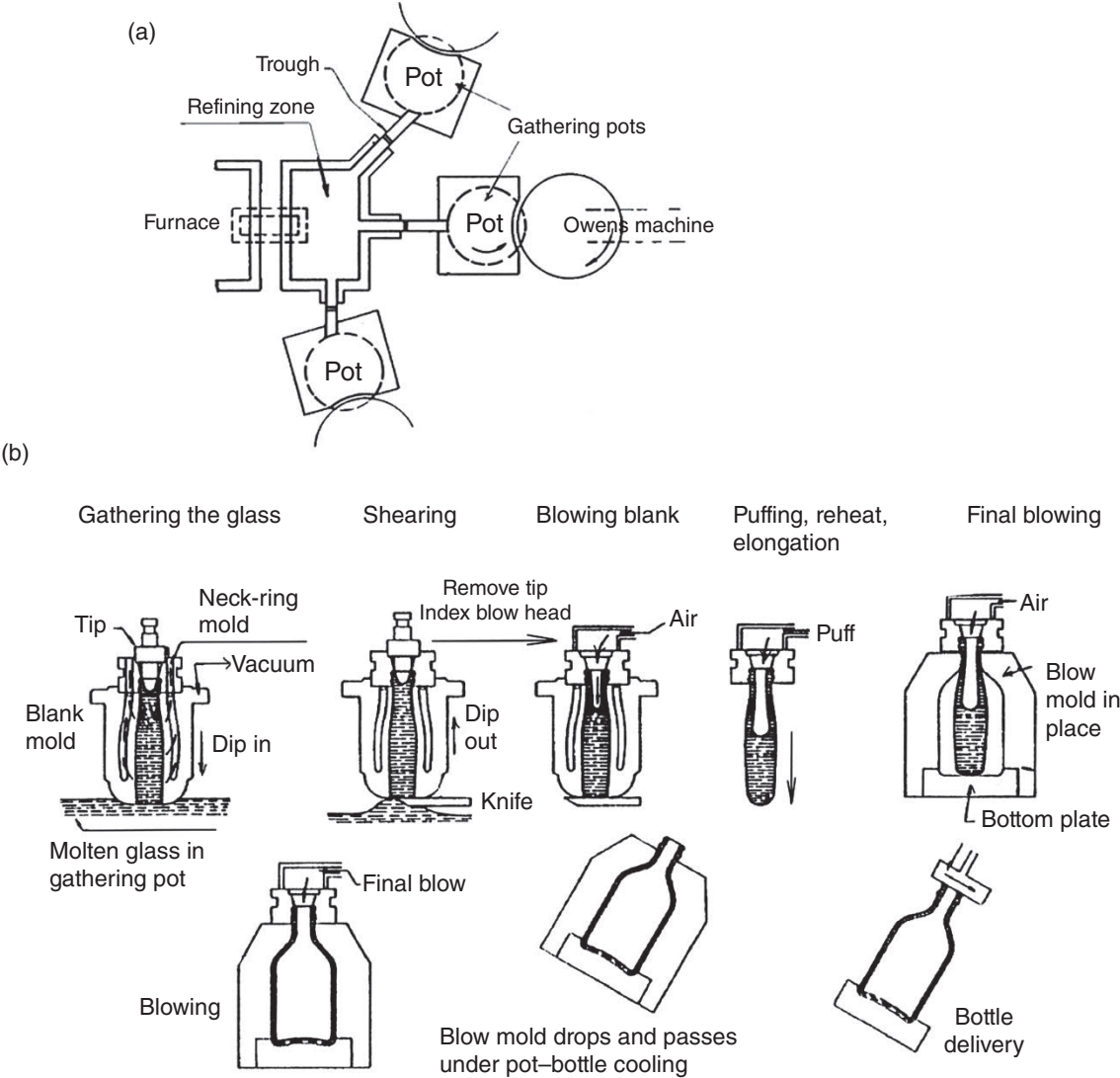


Figure 19 The Owens machine. (a) Heads dipping into the pots as they pass over them while rotating. (b) Its successive steps.

Table 2 Economic efficiencies of Owens-machine and hand bottle forming in 1920 in England (costs in £) [46].

	Owens machine (£)	Hand (£)
Coal	0.149	0.198
Electricity	0.013	0.004
Wages furnace	0.020	0.026
Wages bottle making	0.026	0.385
Repairs	0.037	0.048
Royalties	0.013	0
Interest on capital	0.009	0
Other costs	0.323	0.389
Total	0.724	1.157

Table 3 Advantages of automated forming machines in the United States in 1927 [23].

Ware	Productivity increase	Labor cost decrease (%)
1 pint Whisky	742	90
5-gal carboy	994	83
1 quart milk	1449	95
0.5 pint soda	1149	95
4 oz. pharmaceutical	4110	97

long as bottles had thick bases, the problem was not very serious. When lightweight bottles appeared and spread, however, it became an important disadvantage as did the limitations on the design of parison molds resulting from the need to gather the right amount of glass by the mold.

5.5 The “Gob” Feeder, the Hartford-Fairmont Gravity Feeder (1915)

Progress toward the final solution was much slower in the evolution of the devices now called “feeder” in modern factories. The primitive “flowing stream” of molten glass needed to be controlled to render it intermittent and to separate it into lumps of charges suitable for entering the blank or parison mold of the forming machine. Numerous attempts were thus made to avoid the possible defects created by a stream of glass flowing into a mold or receptacle. These defects were resulting from the coiling, folding, or lapping upon itself of the flowing glass that were leaving disfiguring marks on containers. Because the surfaces of the coils or folds were chilled by contact with the relatively cooler atmosphere and cooler metal of the mold, the defects usually were taking the form of air bubbles or blisters and vein-like creases or depressions.

Efforts were thus made to handle the glass under more viscous or pasty conditions as done with hand-gathering methods. Instead of letting a fluid melt flow by gravity from the tank, the idea prevailed that it was better to impel, drive, or force a viscous liquid from an extension of the tank from which it could not otherwise flow or escape spontaneously too readily. This new *propulsion principle* was implemented in the Hartford-Fairmont feeder (Figure 20). A fire-clay “paddle” was employed for propelling or ejecting glass in timed surges or waves over a fireclay lip or dam such that the ejected glass formed a compact and cohesive charge, the gob, by a reciprocating needle or plunger situated over the hole delivering the gob to the machine.

A peculiarity of this feeder was to deliver glass at the working temperature, which was reached at the end of a long chamber where it cooled down after exiting the furnace. It was first designed in 1915 by Karl E. Peiler of the aforementioned Hartford Fairmont Company (which became Hartford Empire and is today Emhart) [21, 33, 48]: the feeder (forehearth) ended up in a lip beyond which the extrusion orifice was placed (Figure 20). Dipping into the chamber was a paddle that drove waves of glass of uniform size over the lip by a regular vertical and horizontal back and forth motion. The successive waves were forced through the orifice by a plunger (or needle) moving vertically. Being at the working temperature, the glass formed gobs whose size and

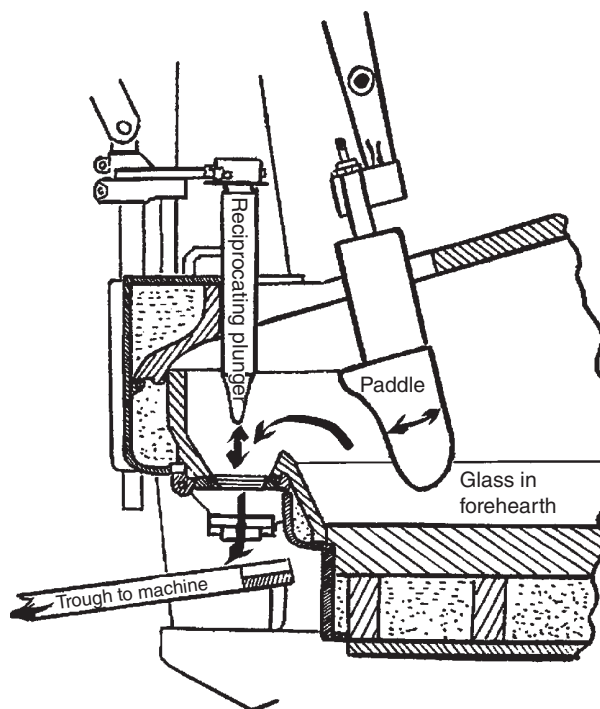


Figure 20 Hartford-Fairmont forehearth.

shape were determined by the length of the paddle stroke and its depth of immersion, the shape of the plunger, and the timing of the various motions.

This feeder might be used to supply either a single forming machine or three or four machines that were served by a hinged receiving trough below the orifice. This trough moved in turn in a *register* with water-sprayed, inclined, cast-iron troughs leading to the machines. The hot gob created a water-vapor cushion on which it rested as it slid down the trough, so tending to prevent deformation [54]. A major improvement in the Hartford-Fairmont feeder (1922) was the disappearance of the paddle that was replaced with a cavity created by a rotating refractory cylinder (tube) set over the orifice [21]: when the plunger rose in the tube, glass was drawn in the tube above the hole; when the plunger went down, a definite quantity of glass was expelled through the hole forming the gob (Figure 20). Hence, the Hartford-Fairmont feeder turned out to have solved the gathering problem that had until then blocked the way to fully automated machines.

5.6 Processing Machines Using a “Gob” Feeder

Referring to Chapter 1.4 for a description of modern container making, it will suffice here to note that the press and blow machines [32] were the first and the easiest machines to operate: the molten glass was gathered and dropped into the parison mold on which the neck-ring

mold was placed. The plunger then entered the molten glass to shape it in the former mold up into the latter where it was chilled. The plunger was removed and the neck-ring mold plus the parison (blank) lifted and transferred in one of the finishing molds. The blowing head was put into position and the bottle was blown to shape, removed, and annealed. But narrow-neck bottles could not be made by this method.

The general solution was to invert the parison mold, the neck-ring mold, and the plunger being placed at the bottom. Glass was dropped in at the top as before, the requisite quantity being cut off with the shears, plugged to shape the neck-ring, given a preliminary blow to form the parison (blank), and then transferred to the blow mold. Multiple molds rotating devices were developed to increase the production. A further improvement in bottle machines of the multiple-mold type was a device for the transfer of the blank to the blow mold, and an apparatus for removing the finished bottle from the blow mold. A number of such devices were invented. The O'Neill, Lynch, and Hartford-Empire machines are some of the best known.

6 Perspectives

As a backdrop to this whole story is a slow evolution of the refractories throughout the ages [55]. With wood-fired furnaces, temperatures did not exceed about 1100 °C so that pots made with sandstone and siliceous clays were adequate. The higher temperatures reached with coal then required more careful selections of clays. But it was only with Bontemps that the need for high purity and high-alumina contents was recognized along with the use of three parts of previously fired clay known as *grog* for one part of fresh clay to limit water contents and ensure much greater strength through better dimensional stability upon firing [19]. This progress and the switch from manual to mechanical pressing of bricks and the adoption of tunnel kilns for continuous firing in the early twentieth century paralleled the evolution of glassmaking and had obviously positive consequences for furnaces of any kinds before the invention of electrofused refractories.

In all branches of industry, the nineteenth century was a *Machine Age* dominated by practical applications of physics and chemistry. Glassmaking was thus no exception, as announced by the *Essay* on this *art* where Pierre Loysel (1751–1813) reviewed in 1799 topics ranging from raw materials and melting reactions to the size of furnaces and the shape of their vaults in relation to a square-law decrease of the heat intensity with the distance from its source [56]. Hence, the emphasis put here on a few

inventors such as the Siemens brothers should not conceal the fact that, in contrast with previous periods, innumerable engineers were at work and secured so many patents for their innovations that the century might alternatively be termed the *Patent Age*. A case in point is the furnace designed in the 1860s in Hannover by Henning Boetius for the manufacture of glass, iron, steel, and other materials. Its main feature was “to keep the bed of the furnace and the side walls of the fire-place cool, and to preserve the same from the destructive action of the heat for as long a period of time as possible” [57]. Thanks to its simplicity, low operating costs and simple control of the fire intensity through valves admitting more or less air, this kind of furnace would be widely used for contained glass until the mid-twentieth century (Figure 21).

In all branches of glass manufacturing, such efforts resulted in the development of mechanization at the turn of the nineteenth and twelfth centuries. Industrial developments were not as fast as they could have been, however. They meant not only a drastic change in factory organization, which did not suit well specialized glassworkers, but also required rather heavy investments at the beginning of the twentieth century when the European glass industry was meeting with difficulties on the American market. Heavy tariffs imposed by the American government on glass imports caused the traditional export market of European companies to collapse within a few years. The crisis lasted until the market was organized via at least two International Conventions for special and plate glasses, which considerably improved the situation.

In 1918, at the end of the war, the need for glass was huge and factories had to resume production as fast as possible. Thousands of glassworkers had disappeared and numerous continental factories had been destroyed. They were rebuilt with integration of mechanical processes that had mostly been designed before the war. As clearly spelled out by the Siemens brothers, the main thrust behind glassmaking improvements had been the achievement of cost reduction, which mainly resulted from the efforts made to improve the energy efficiency of the processes and from the switch from batch to continuous operations. The resulting decrease in the numbers of qualified workers was a constant source of conflict, especially with blowers who had always considered themselves as a kind of labor aristocracy [58]. Of course, these efforts were not interrupted once mechanization became fully achieved in the early twentieth century but were renewed in the last part of the century as a result of rapidly increasing energy costs. To summarize the results achieved, it will suffice to state that the amount of coal burnt was 2.5 times that of glass produced before the regenerative furnace was invented, and now would be 25 times smaller. The continuous nature of the process

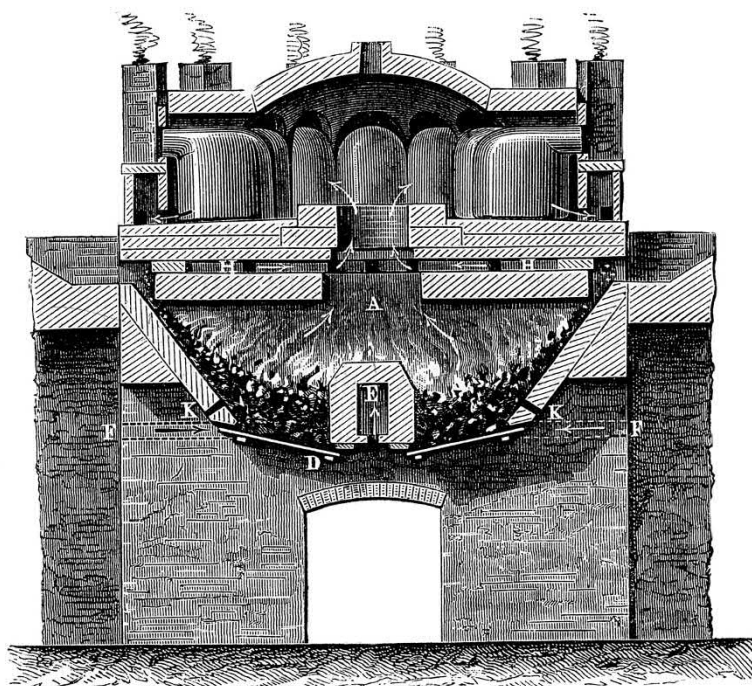


Figure 21 A Boetius furnace for the melting of crystal glass in 12 pots [20]. Coal brought by two lateral openings transforming into coke upon reaching the grids D on which it is gasified before mixing with the preheated air (circulating through the canals F of the regenerator and H of the siege supporting the pots) and burning up to the crown.

largely contributed to this dramatic reduction through quicker operations, faster melting, and, thus, lower fuel consumption.

At the same time, working conditions markedly improved by making close contact of workers with the furnaces and molten material unnecessary. One of the main reasons why Boucher invented his machine was his concern for the health of workers who were suffering from eye, throat, and lung diseases under difficult conditions of the workshop where sharing of blow pipes by workers was the rule. Ironically, his invention initially caused social unrest among glassblowers who were fearing to lose their jobs. In the end, however, the improvement he brought them earned him in 1902 a price of the French Academy of Sciences. The situation was not peculiar to France [59]. But speedier and more economical means of production led to a greater demand for the output so that wages increased instead of decreasing as exemplified in Saint-Gobain where the average yearly wage increased from 530 to 1530 francs from 1830 to 1910 [42]. This obstacle removed, progress toward a higher state of development of machinery in glass factories was much more rapid. The numbers of blowers did decrease markedly, however, from over 6000 in the United States in 1896 to about only 1000 in 1924 for a production that tripled during the same period [53].

Another important feature was the dynamical nature of both production and markets as currently illustrated by the development of glassmaking in Asia (Chapter 9.6).

Particularly noteworthy in this respect was the very rapid development of flat glassmaking around the city of Charleroi in Belgium throughout the nineteenth century [60], which was fostered by the local availability of coal and good sand, a central geographical location, and innovative engineers exemplified by D. Bievez or É. Fourcault who designed at the beginnings of the twentieth century the first process from drawing directly flat glass (Chapter 1.4). With a production that was exported all over the world, however, this industry was highly sensitive to increases of its labor and coal costs and to abrupt changes in tariffs imposed, for instance, by the United States, an important market.

To conclude this short review, it is appropriate to note that the three centuries of efforts that resulted in the continuous production of plate glass were almost instantly ruined by the invention of the float process, which has become a textbook example of *disruptive* innovation. There is in fact some analogy with the old-age oil lamp, which took more than two millennia to become fully optimized just a century before being made obsolete by the electrical lamp (Chapter 6.9). Glass remained a fundamental component of the lighting device, however, actually the only one common to both of them.

N.B. A passage of the *Annals* of the Byzantine chronicler Niketas Choniates (~1155 to ~1216) has come to our attention after the present chapter was written. Glass historians might be interested in knowing that, when his astrologers predicted apocalyptic winds, the emperor

Manuel Komnenos (r. 1143–1180) “sought caves and hollows as protection against the winds and prepared them for habitation; he removed the glass from the imperial buildings so that they should not be damaged by the blasts of the winds while his attendants, kinsmen and sycophants also anxiously involved themselves in these undertakings, with some burrowing into the earth like ants and other making tents, fastening them with threefold cords and cutting sharp pegs to serve as supports” [61]. The story is similar to the Duke of Northumberland’s [3], but has the great interest of antedating it by four centuries.

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10.10

Glass, the Wonder Maker of Science

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1 Introduction

Glass was first the preserve of elites of the Late Bronze Age (Chapter 10.2). Its variety of vivid colors was clearly distinguishing it from other man-made materials and even allowed glassmakers to imitate highly prized gemstones [1]. Its chemical inertness, tightness to air, and limitless shapability were then put to good use in many kinds of vessels when blowing of transparent glass became common toward the beginning of our era (Chapters 10.3, 10.5). Along with optical isotropy, these properties made glass the science material *par excellence*. Without any overstatement, one can even claim that science as we know it would not have existed without glass. Of course, other kinds of materials have participated in the scientific enterprise but none of them, to begin with metals such as copper and mercury, have played a comparable key role.

The claim is obvious for optics whose laws required not only transparent, but also isotropic solid materials to be established. “It is with the prism that Newton anatomized light, and stole this knowledge to the celestial intelligences that alone had it before him,” gracefully acknowledged the famous *Encyclopédie* [2] of Diderot and D’Alembert in the eighteenth century. As also stressed by the *Encyclopédie*, it was in addition certain that, “ever since the discovery of metals, Chemistry did not make a more marvelous and useful discovery than that of glass.” It is actually well known that, as early as in Antiquity, the two fields of optics and alchemy were the first ones that emerged thanks to glass. At least to some extent, however, it would be difficult to find a single branch of science that did not rely on glass.

This statement remains true even if one discards its ancillary uses in spectacles, lamps, or clocks and

especially in microscopy slides or photography plates, without which much work could not have been done, or neglect the bubble level invented in 1661 (description in 1666) by the polymath and diplomat Melchisédech Thévenot (1620–1692) [3], which was soon after appended to many kinds of precision instruments. Actually, it is not commonly acknowledged that in two different ways the use of glass was a major driving force behind the Scientific Revolution of the seventeenth century. First, it was glass lenses that induced a complete change in man’s worldview by having made the exploration of infinitely large and small possible with the telescope and the microscope, respectively. Second, although emphasis regarding the Scientific Revolution is usually put on mechanics and on its mathematization, one should not overlook that glass also gave physics and chemistry a sounder quantitative basis through the definitions and measurements of the fundamental variables of temperature, pressure, and different electric charges, the study of air pressure having in particular settled for good the fundamental question of the existence of vacuum.

Of course, glass thermometers and barometers have now been replaced with electronic devices, but the advances made in glass science and technology illustrated by a great many chapters of the Encyclopedia have never ceased to be exploited in scientific endeavors. A striking example is that of pH meters, which, after chemical optimization of their glass electrodes, have become from the late 1930s the chemical instrument most widely employed in academic, industrial, and natural contexts (Chapter 5.8).

Without any claim to comprehensiveness, this chapter thus aims at illustrating the fundamental importance of glass for science. Optics will first be dealt with, followed by alchemy and chemistry. Through temperature and pressure, two of its intensive variables, physical chemistry will then be considered. Finally, a brief review of electrical

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research will illustrate how, from the discoveries of mercurial light and two kinds of electric charges in the early seventeenth century, glass led to the birth of subatomic physics at the beginning of the twentieth.

In preamble, it is useful to recall that the term *science* is anachronistic to describe activities in the past. Being a derivative of *scio* (I know), the Latin term *scientia* was designating a rational knowledge based on firm foundations. As an early translation of the Greek term *philosophia* (*love of wisdom*), it gave rise to the expressions of *philosophical*, *moral*, or *religious* sciences. The Latin term closest in meaning to the modern *science* was *disciplina* (action of learning) whereas the term *art* (*ars*) also took on a broad meaning to designate, as the Greek *tekhnè*, any trade or human know-how practiced by *artists*. From Isaac Newton (1643–1727) to William Thomson, better known as Lord Kelvin of Largs (1824–1907), savants thus traditionally considered themselves as *natural philosophers* and their practice as *natural philosophy*. In the English-speaking world, they became very lately *scientists*, after this term was coined by the Anglican priest and polymath William Whewell (1794–1866) (e.g. [4]).

2 The Source of Optics

2.1 The Study of Refraction

The earliest optical observations likely involved the still surfaces of ponds onto which the landscape was reflecting and through which partially immersed straight poles or oars showed a marked kink at the interface with the air. Dating back to the mid-eighth century BCE in Mesopotamia for the earliest, intriguing lens-shaped pieces of rock crystal (quartz) or glass have been found in the archeological record [5, 6] but their use as magnifying glasses seems unlikely, in agreement with the fact that it is not documented in the ancient literature [6]. Better known were reflection and refraction effects, such as a fire kindled by a beam of light passing through a glass filled with water, which could have been commonly observed with the vessels and vases present in every household when transparent glass became a commodity in the Roman Empire (Chapter 10.3). The Latin philosopher Seneca (4 BCE–65 CE) thus reported that “writing, however tiny and difficult, is seen larger and clearer through a glass full of water” and even that “the stars themselves seem larger if one looks at them through a cloud” [7]. In agreement with the ideas of the period, however, Seneca added that the “eyesight falters in moisture and cannot reliably grasp what it wants to” especially because images were distorted at the same time they were enlarged.

The concepts of *ray of light* and *reflection* had been formulated early through the study of mirrors, in particular, which were made up of metals. Glass thus entered the scene only with the experimental study of refraction performed by Claudius Ptolemy (second century) in Alexandria [8], the stronghold of Greek science, which happened to be close to the main areas of production of Roman glass (Chapter 10.3). Like his Greek predecessors, Ptolemy did not try to understand light itself in geometrical terms, but what the eye was seeing. His interest in refraction was thus closely related to his astronomical work [9], for which he is best known since the geocentric system of the world expounded in his *Almagest* would remain basically uncontested for nearly 15 centuries.

With a graduated brass disk similar to that used for his astronomical observations, Ptolemy measured angles of refraction at three interfaces, namely, air–water, air–glass, and water–glass (Figure 1). He then reported in his *Optics* that refraction occurs “not only in the passage from rarer and more tenuous to denser media — as happens in the case of reflection — but also in the passage from a denser to a rarer medium” in such a way that the angles of incidence and refraction “do bear a certain consistent qualitative relation to one another with respect to the normals.” Possibly because he did not observe a constant ratio between the angles of incidence and refraction (Figure 2), Ptolemy contented himself with stating that this ratio increases with these angles. Deviations of his data from the theoretical values (Figure 2) make it in fact likely that he corrected his observations by 0.5° at small angles and by 2° near 80° such that, in modern notation, the differences between two successive measurements were following relationships of the form $\theta_r = a\theta_i - b\theta_i^2$ between the angles of refraction (θ_r) and of incidence (θ_i) [10]. Would it be indicative of an influence of Babylonian mathematics, which relied heavily on such arithmetical progressions? Whether or not this was the case, Ptolemy’s measurements look surprisingly modern, contradicting the common opinion that experimental work was ignored in Antiquity. But their results did not translate into any application. On the one hand, the effects of refraction were rather thought to be problematic whereas, on the other, Ptolemy and his fellow astronomers were primarily interested in the noble and divine harmony of celestial movements.

Ptolemy’s *Optics* is actually known through a twelfth-century Latin translation of the Arabic version, which was then lost like the Greek original. It was in Islam that further progress was made in optics, especially by Ibn al-Haytham (965–1040), better known as Alhacen in the Latin West. In his own *Optics* [11], this astronomer and mathematician was also interested in vision but his main

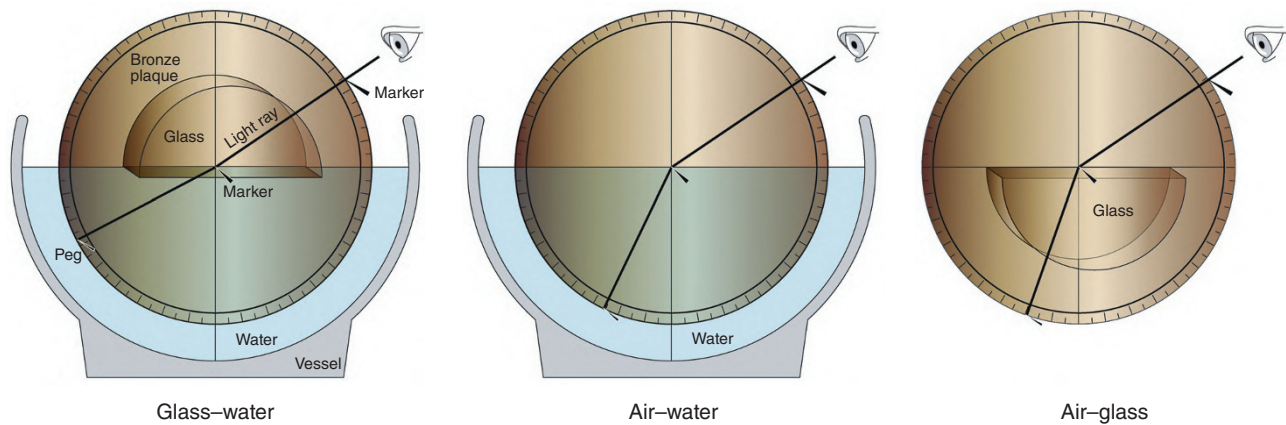


Figure 1 The concept of ray of light at the basis of Ptolemy's study of refraction between air, water, and glass: angles of incidence of rays measured with a graduated bronze disk as a function of angles of refraction set by a marker placed at the center of the disk and a peg repeatedly moved by 10° . Set up reconstituted in [9].

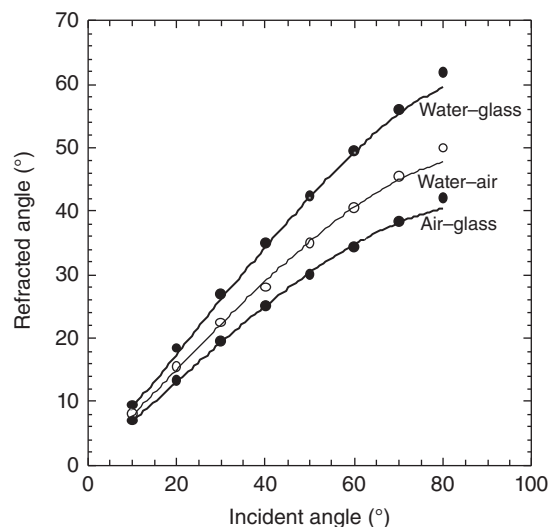


Figure 2 Anachronistic geometrical representation of Ptolemy's refraction measurements between air, water, and glass [8]. Data calculated from Snell–Descartes law included for comparison (curves) with refractive indices of 1.33 and 1.52 for water and glass, respectively.

innovation was to consider light as an independent physical entity that had to be investigated geometrically for its own sake. In Book VII of his treatise, the principle of the magnifying lens was in particular clearly described: “if an object is placed in a dense spherical medium of which the curved surface is turned towards the eye and is between the eye and the centre of the sphere the object will appear magnified” [11]. But glass did not become the basis of any optical devices. Al-Haytham's *Optics* itself was even largely overlooked since a single ancient manuscript has transmitted its entire original Arabic text.

2.2 The Marvels of Refraction

It was through its Latin translation probably made at the turn of the twelfth and thirteenth centuries that al-Haytham's *Optics* did find interested readers, among them the visionary Franciscan friar Roger Bacon (~1217–1292). By then it had been understood that changes in images are determined by the shape of the glass pieces through which an object was seen, and not by some intrinsic virtue of the material. Optical applications had, therefore, become possible. In his own *Optics* illustrated with many diagrams, which he included in his *Opus maius* (*Great Work*), Bacon thus wrote that “We can so shape transparent bodies, and arrange them in such a way with respect to our sight and objects of vision, that the rays will be refracted and bent in any direction we desire, and under any angle we wish we shall see the object near or at a distance” [12]. In other words, Bacon understood that refraction was the key phenomenon that would make any kind of visual effect possible as angles, and not distances, were the basic parameters to be dealt with. Because of refraction, convex lenses, for example, cause a parallel beam of light to converge at a point, the focus, which is closer the stronger the curvature (Chapter 6.1). Conversely, concave lenses make it to diverge. By combining these two types of lenses, it was possible to make the light follow any desired path. As stated by Bacon,

Thus from an incredible distance we might read the smallest letters and number grains of dust and sand owing to the magnitude of the angle under which we viewed them, and very large bodies close to us we might scarcely see because of the smallness of the angle under which we saw them,

for distance in such vision is not a factor except by accident, but the size of the angle is. In this way a child might appear a giant, and a man a mountain.

Although it took a few centuries to design the telescope and microscope anticipated by Bacon in his book, which was widely read, it is probably no coincidence that the first spectacles were invented at his own time, in Tuscany, to correct far-sightedness with convergent lenses [13] whose optical quality did not need to be very high. Thanks to the isotropy of its optical properties and relative ease of production, glass rapidly proved to be more appropriate for optics than crystals such as quartz and beryl, which were also used early (beryl having yielded the German word *brille* for spectacles), whereas a new mode of machining also helped, which consisted in polishing the lenses with spherical tools of the curvature that was desired.

Shortly afterward glass was involved in other noteworthy experiments made by the Dominican friar Dietrich of Freiberg (~1250–after 1310) to understand the nature of the still elusive rainbow [14]. Using glasses filled with water to simulate the propagation of light within a single droplet arrested in its fall, Dietrich masked various parts of the vases illuminated by the sun to find out that light undergoes a first refraction when entering a droplet, then a reflection when reaching its rear, and finally a second refraction when leaving it in the direction of the observer (Figure 3). By raising and lowering slightly the vases, Dietrich also noticed changes in the color of the ray and concluded that each color seen by the observer is coming from a number of neighboring droplets. Finally, the secondary rainbow sometimes seen above the primary could be explained in terms of a double reflection of rays entering a droplet near its top, which made these rays leaving it

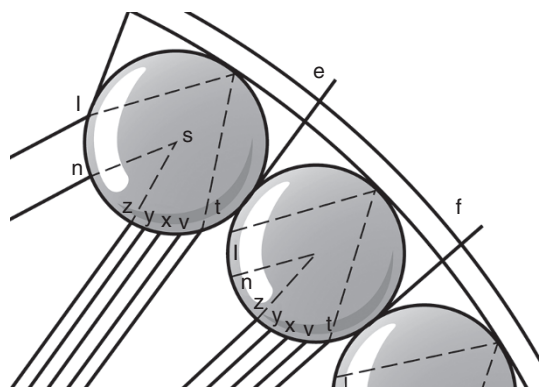


Figure 3 The rainbow as understood by Dietrich de Freiberg: parallel light of the sun entering water droplets from the left and leaving it toward the observer's eye after a first refraction, a reflection and a second refraction. Part of an original sketch [14].

upward in the reverse order of colors as compared with the primary rainbow, and with a much reduced intensity due to the relative scarcity of such double reflections. Interestingly, similar experiments were made at the same time in Iran by the mathematician al-Fârisî (1267–1319), who arrived at similar conclusions in his *Revision of Optics*.

2.3 The Exploration of the Universe

Because they were more difficult to shape, divergent lenses were not developed until the sixteenth century to relieve myopia when, resulting itself from a markedly growing need of books, the invention of the printing press had in turn enhanced further book reading. It is probably not fortuitous that the telescope was invented when these lenses became common. Chance likely played some role in its invention. According to tradition, the first step was made in the Netherlands in 1608 when a lens maker, Hans Lippershey (1570–1619), asked for the exclusive right to sell an instrument with which distant objects appeared larger and distinct. When two spectacle makers contested Lippershey's request, the rumor of such an interesting invention had in fact already spread so quickly that the instrument itself had reached Rome and was sold in some Parisian spectacle shops in the spring of 1609. Actually, the story cannot be told that simply. The fact that Middelburg, Lippershey's hometown, was at that time a thriving glassmaking center, which was producing the highest-quality products of the Dutch Republic was unlikely coincidental [15]. But the invention of the telescope cannot be assigned to any single person: rather, it represented the outcome of long evolution in which progress made in lens grinding in the early sixteenth century played in particular a considerable role [15].

This complexity notwithstanding, Galileo Galilei (1564–1642) heard of the instrument while being in Venice in July 1609. He hastened to make his own by grinding and polishing two kinds of lenses, concave for the ocular and convex for the objective, and placed them at both ends of a wooden tube about 1 m long (Figure 4). As a reward for the military value of his *occhiale* (spectacles, in Italian) or *perspicillum* (from the latin *perspicio*, to see clearly), the *Serenissima Repubblica* offered Galileo a highly paid faculty position, which he eventually declined. Quickly, however, the idea came to him to use the *spy-glass* for something completely different than checking the enemy sails: to peer carefully into the heavens.

Although observations were made difficult by a narrow field of view and the need to keep the eye stuck to the eyepiece, countless unknown stars were seen, four satellites of Jupiter discovered and the rugged surface of the Moon ascertained and depicted. Following by 67 years the *Revolutions of the Heavenly Spheres* of Nicolaus Copernicus



Figure 4 The objective of Galileo's telescope. These instruments had a typical magnification of 20, as given by the ratio between the focal lengths of objective and ocular lenses, a field of view of about 15 arc min and a resolution of 20 arc s [16]. Apertures of the ~45 mm convex and ~20 mm concave lenses reduced with cardboard rings by up to 50% to minimize optical aberrations. Source: Photo Franca Principe, Museo Galileo, Florence, inv. 20121.

(1473–1543), Galileo's *Messenger of the Stars* [17] quickly published in March 1610 unveiled these epoch-making discoveries and gained its author a high European reputation. In further observations, Galileo detected the strange appearance of Saturn, spots at the Sun's surface, and the phases of Venus. But the main outcome of his work was that two small glass lenses had shaken into pieces the ancient Aristotelian cosmos, finite, immutable, and hierarchically ordered, bounded by the perfect sphere of fixed stars and centered on the most humble Earth [18]. As stated by Copernicus, the Earth was instead one of the planets orbiting the Sun, and Galileo also concluded that the fundamental distinction between the corruptible terrestrial matter and the immutable *quintessence* of the heavens had to be forgotten.

2.4 Practice vs. Theory: Some Real Problems

To improve income and satisfy the curiosity of Princes and wealthy amateurs, Galileo polished countless lenses and sold dozens of telescopes (but avoiding to do so with potential competitors!). A great many seventeenth-century scientists did the same, but all shared the difficulty of finding good glass. With an index of refraction of about 1.52 and a low dispersion (Abbe number of about 60, cf. Chapter 6.1), the *crown* glass used in optics was plain window glass, deriving its name from the eponym process (Chapter 10.8). But it was suffering from a great many defects, namely, streaks, striae, veins, or tails caused by inadequate annealing, chemical heterogeneities, or contamination of the melt by the pots, by the marble plates on which gobs were rolled or by dirt, which

would have been very difficult to eliminate even with the much higher melting temperatures reached in modern furnaces (Chapter 1.2). Hence, the physicist Nicolaas Hartsoecker (1656–1725) still deplored in 1694 in his *Traité de dioptrique* [19] that “out of more than two hundred large glass plates that I polished with great care, I could only find two reasonably good and five fair” to be used for his own microscopic observations, of animal semen in particular.

Following briefly Galileo's work, the law of refraction had been formulated (without demonstration) by the mathematician and astronomer Willebrord Snell (1580–1626) in the early 1620s. As indirectly known [20], it stated that

If the eye O (in the air) receives a light ray coming from a point R in a medium (for example, water) and refracted at S on the surface A of the medium, then O observes the point R as if it were at L on the line $RM \propto$ surface A . Then $SL:SR$ is constant for all rays.

In mathematical terms, the law states that $\sin r: \sin i$ is constant, where i and r are the angles made by OS and SR with the normal to A at S . As demonstrated by René Descartes (1596–1650) in his *Dioptrique* in 1637 [21], the ratio between the sines of the angles of incidence and refraction of light between two media is indeed constant. This constant was lately defined as the *refractive index* by the polymath Thomas Young (1773–1829) to characterize the relative ability of a medium to deflect light. Without this definition, however, Snell-Descartes law had already made in principle possible to calculate the shape to be given to lenses to improve instruments and obtain the desired effects. No matter how carefully lenses were prepared, however, images were increasingly blurred when the magnification was increased. This effect would be termed *chromatic aberration* when later understood (Chapter 6.1).

This aberration problem was the main one to be faced in the design of telescopes and microscopes. Although Galileo himself saw flies looking as big as lambs with his instrument, an inverted telescope is not a microscope: its field of view is much too narrow because the divergent light coming from an object at very close distance cannot be focused like the parallel light emitted by a distant star. Built in the Netherlands on a scheme established by the astronomer Johannes Kepler (1571–1630), the first *compound* microscopes closely followed the telescope. They had two convex lenses whose distance was varied to change the magnification. But it required a few decades for the observation of small things to lead to great discoveries. Although glass corrects vision, it distorts it still more easily. Even at moderate magnifications where

chromatic aberration is not yet detrimental, observations are especially tricky when the object has to be illuminated, the focus delicately achieved and small lenses prepared to produce sharp images. In addition, Nature had to be examined directly assured the old scholastic tradition whose vestiges maintained a certain distrust toward the microscope.

2.5 An Astonishing Microscopic World

One of the first to overcome a good part of these difficulties was the physicist Robert Hooke (1635–1703) with the 30–40 magnification of his microscope described in 1665 in *Micrographia* [22]. His instrument comprised two lenses placed in a 20-cm long cardboard tube whose distance was varied with a thread engraved in a wooden support, while the light of an oil lamp was focused on the observed specimen by a spherical glass bulb filled with water (Figure 5). His experiments were made with various kinds of lenses and with “waters, gums, resins, salts, arsenic or oils.” As Hooke concluded in his preface, however, none are “more useful than that which is made with two glasses.”

But the true appearance of the specimen observed was difficult to ascertain because “the aperture of the object glasses are so small that very few rays are admitted and [...] the object appears dark and indistinct.” As a result, emphasized Hooke, who was first trained as a painter, “I never began to make any draught before, by many examinations in several lights and in several positions to these lights, I had discover’d the true form.” A mix of pure science and popularization, *Micrographia* also created sensation with its great many careful drawings, which, for instance, revealed the highly complex nature of fleas and flies, and with Hooke’s perspicacious comments. These led him in particular to coin the word *cell* for describing the small lodges observed in thin slices of wood, and to interpret the geometrical shape of crystals in terms of the arrangement of minute particles (Figure 5).

Like telescopes, microscopes diversified quickly [23] but magnifications higher than about 40 could not be achieved with the various kinds of compound instruments designed. It was with a miniature version of the magnifying glass that a magnification of up to 270 and a resolution close to 1 μm were reached by the self-taught Antoni van Leeuwenhoek (1632–1723). Apprentice in his youth to a cloth merchant before becoming a bailiff and surveyor in Delft, Leeuwenhoek took his inspiration from the instrument used by drapers to inspect fabrics. In a way that is still elusive, his convex lens was carefully ground and polished from a glass globule a few millimeters in diameter. It was clamped between two perforated metal plates 5 cm long and 2.5 cm wide to which was attached

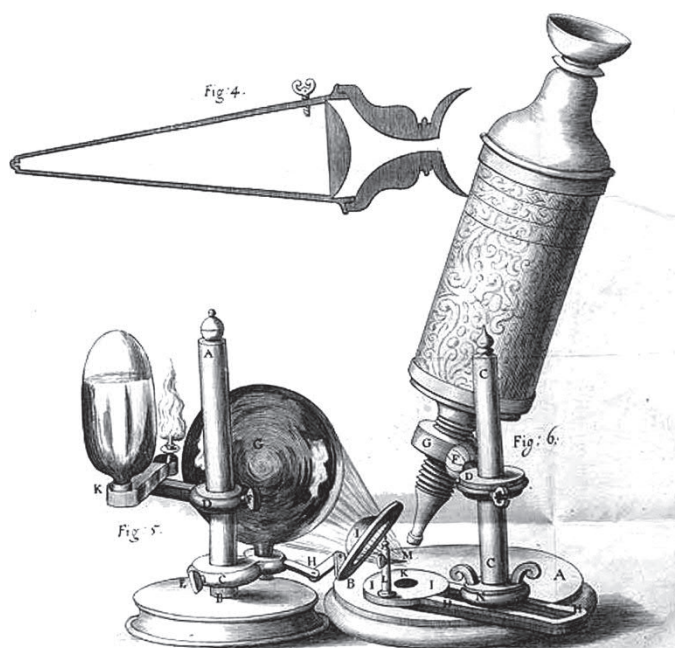
the sample holder, which could be rotated in the three directions of space. The sample could thus be brought conveniently and stably into focus, which had to be done next to the eye because of the very short focal length of the lens.

When he died, Leeuwenhoek left 247 microscopes mounted and 172 replacement lenses. As early as 1674, he understood that many of the microscopic things he was the first to observe were animals because they were moving freely. Spontaneous generation did not exist, he then demonstrated by describing bacteria and protozoa as well as spermatozoa of species ranging from mollusks to mammals (Figure 6). Dealing also with observations of nerves, muscular fibers, hair, elephant skin, snail eggs, bee legs, plant seeds, gunpowder, or salts of wine and vinegar, about 100 letters were written from 1676 to 1723 to be “Englished” for publication in the *Philosophical Transactions of the Royal Society* [25], which had been founded in 1665. Relative to a scale of size whose units were a sand grain, a beard hair, or a red globule, it was a whole new world replete with minute strange features and tiny living beings that Leeuwenhoek’s lenses revealed to the learned world.

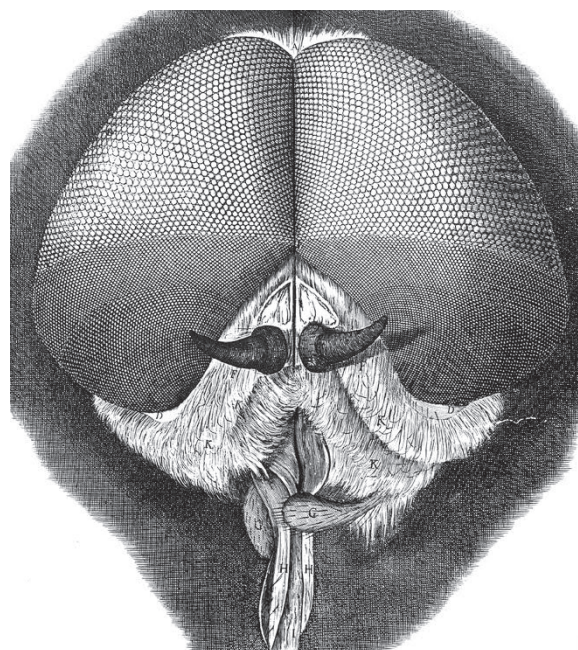
2.6 The Anatomy of Light

In the form of “a small rod, grooved, or angular,” as also noted by Seneca [7], glass had the intriguing peculiarity of emitting “the kind of color seen in a rainbow.” In his room in Cambridge, Newton was struck in 1666 by the elongated shape of the rainbow produced by such a glass prism. A quick check showed him that this feature did not result from some defect of the prisms, which were “free from veins” and had their sides “accurately plane and well polished without those numberless waves or curls which usually arise from sandholes in polishing with putty” [26]. And light does not propagate along a curved path, noted Newton in his first paper on the subject [27], as done by “a tennis ball, struck with an oblique racket.” A series of experiments eventually led him to an *Experimentum Crucis*: after refraction by a first prism, red and orange rays were, for instance, refracted in the same way by a second prism with refrangibilities increasing again from red to violet. It followed that “whiteness is the usual colour of light, for light is a confused aggregate of Rays imbued with all sorts of Colors, as they are promiscuously darted from the various parts of luminous bodies [...] but if any one predominate, the light must incline to this color.” Newton then explained that images are blurred at large magnification because the focal length depends on light color, increasing from violet to red. It was the cause of the *chromatic aberration* of lenses, which he thought could not be corrected [26].

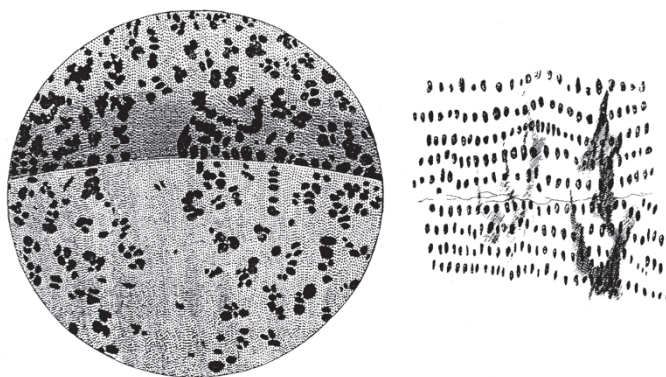
(a)



(b)



(c)



(d)

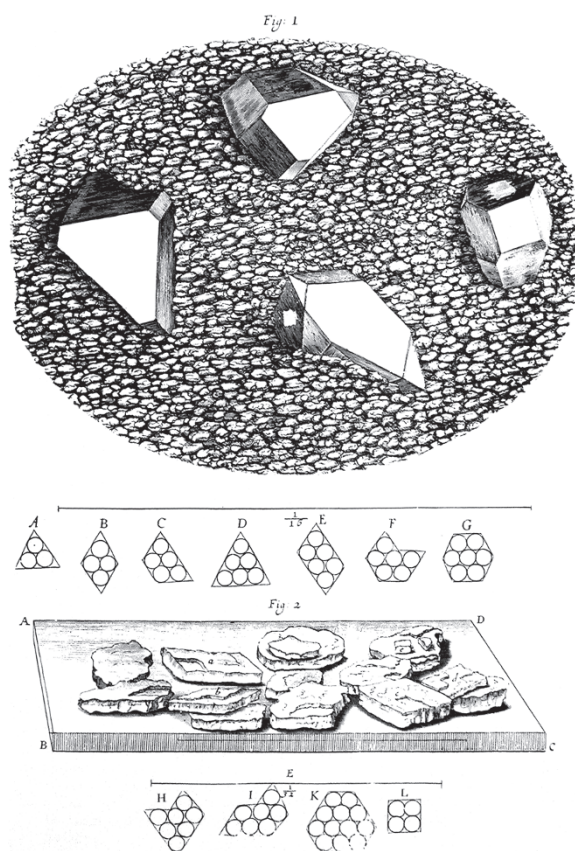


Figure 5 Some of the astonishing features revealed by Hooke in *Micrographia* [22]. (a) His compound microscope, drawn in longitudinal view on top left. (b) The remarkably complex compound eye of the fly. (c) The *cells* visible in wood coal. (d) The geometrical shape of crystals assigned to the regular arrangement of tiny spherical particles.

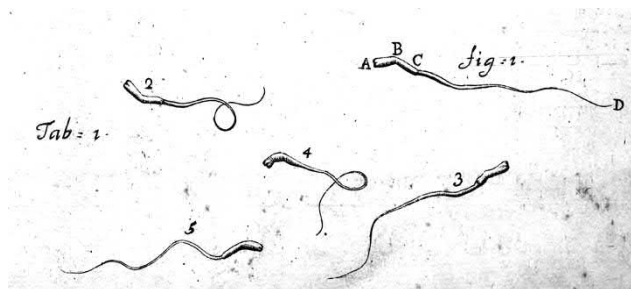


Figure 6 The *Animalcula* discovered in the *Semine masculino* of a cock, each having a “long and exceedingly small tail” not readily observed under the microscope by Leeuwenhoek who marveled at “an infinite number of those *Animalcula*, swimming in legions together, and crossing one another like clouds in a stormy day, and as brisk and lively as if the cock had been newly killed” [24].

2.7 Flint Glass: The Advantages of a New Composition

Glass eventually brought a solution to chromatic aberration. The starting point was the lead-bearing compositions that began to be made in England when a royal *Proclamation* forbade in 1615 the use of wood in melting furnaces (Chapter 10.9). Because of less efficient heating by the smaller flames of coal, some minimum (Pb_3O_4) was added to the batch to lower melting temperatures in pots that had to be covered to prevent reaction of the fumes produced with the melt. Because of lack of sand with low-enough Fe contents in England, high-purity flint became the silica source used and gave its name to the new glass. In 1674, the investor and dealer of Venetian glass George Ravenscroft (1632–1683) secured a patent for the *Manufacture of crystalline glass resembling rock-crystal* [28, 29]. He did not invent the new composition, however, but rather promoted it by having in particular the process modified to prevent the glass from crizzling under the action of humidity.

Owing to a higher density (e.g. 3.0 g/cm^3 for 30 wt % PbO), flint has a high refractive index of 1.60 or more and is in addition more dispersive than crown glass (Abbe number lower than 50). These properties made it valuable in optics especially after the mathematician Leonhard Euler (1707–1783) had theoretically shown in 1747 how chromatic aberration could be corrected, as done by the eye, by a juxtaposition of differently refractive media. Although first unconvinced by Euler’s demonstration, the optician John Dollond (1706–1761) eventually showed in 1758 that he could cancel out the aberration by associating a concave flint and a convex crown lens with focal distances in 2 : 3 ratios. (A similar arrangement had in fact already been realized toward 1730 by the lawyer Chester Moore Hall (1703–1771), who did not publicized it.) Shortly afterward, Peter Dollond (1731–1821),

John’s son, improved the design by inserting a convex flint lens between two concave crown lenses so that a wider field of view was combined with a reduction of another defect, the spherical aberration (Chapter 6.1).

But grinding and polishing of lenses remained a difficult exercise for which the theory also written by Euler found few readers. Empiricism was still predominant. Peter Dollond “makes at once a large number of lenses from both glasses, and combines them until he finds an assortment with which he is satisfied,” was thus told the mathematician and astronomer Jean Bernoulli (1744–1807) during a visit to London in 1769 [30]. National considerations were in addition lurking at a time when Venice was declining and England was benefitting from a monopoly situation for its flint. A nationalistic feeling was thus felt in London by Bernoulli, who commented:

When the glass has been prepared in the glass-works [...], it is rolled into hollow cylinders in which the opticians whom one wants to favour can easily make a choice of the best glass; but after that, one melts the remaining cylinders and out of them one makes flat but rough masses, where no one in the world can see whether or not there are bubbles or streaks in the glass. Foreign artists can hardly flatter themselves to obtain another glass than the latter, and if the maker knows that glass is requested to imitate an invention of his country, it will not be up to him that one gets it as bad as possible.

2.8 Seeing Farther: The Issue of Glass Homogeneity

The general quality of flint remained poor because the usual imperfections of glass were compounded by the difficulties faced to incorporate homogeneously the dense lead oxide at high concentrations, which resulted in glass layers of increasing PbO contents from top to bottom in the melting pots. In the last part of the eighteenth century, the new French and German producers that had entered the market in the meantime met with the same problem. The solution was brought only around 1790 by Pierre-Louis Guinand (1748–1824), a former apprentice carpenter from the Neuchâtel area in Switzerland, through vigorous stirring of the molten batch with the refractory rod he invented (Figure 7). The interest raised by the high-quality lenses of up to 20 cm obtained by the new process led Guinand to be hired in 1805 in Bavaria. There, a collaboration began with the young physicist Joseph von Fraunhofer (1787–1826) who would build in 1824 the first modern achromatic refracting telescope

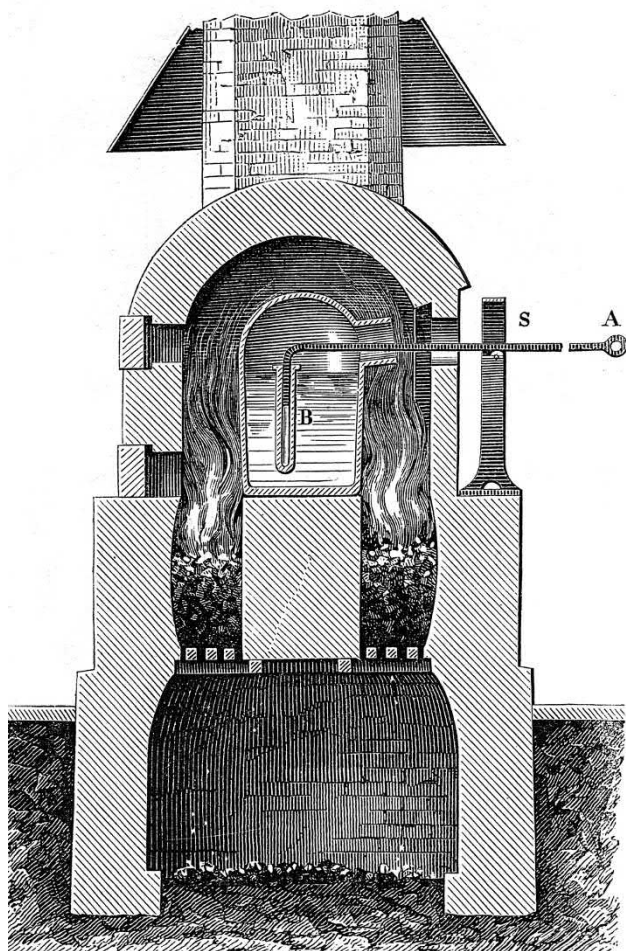


Figure 7 Guinand's process: stirring of molten flint with a U-shaped iron bar embedded into a refractory mantle made of the same earth as the covered pot [31].

with a 24 cm lens at the Russian Dorpat observatory, in Estonia.

This markedly better flint was thus making it possible to increase the size of lenses to see farther in the universe by gathering more light. Whereas lens diameters were a few cm at Galileo's time, they reached 1.02 m in 1890 at Yerkes Observatory (Wisconsin). But there was a limit in this increase because larger still lenses would have been too heavy to be supported by their edges, and less sensitive for observations in blue light for which long photographic poses (on glass plates) showed their superiority over visual observations. Again, glass was the solution to this problem. To avoid chromatic aberrations, Newton had proposed to collect and focus the light not with a lens, but with a convergent mirror [27, 28]. Although this design allowed William Herschel (1738–1822) to discover 2500 new nebulae (Chapter 7.1), the construction

of large *reflectors* was difficult because a mirror must have a polish four times smoother than that of a lens and is in addition more sensitive to vibrations, thermal expansion, and other disturbances. When a 1.83 m metal mirror was polished in England in 1845, it was thus thought that the limit of feasibility had been reached.

It was a new process of silvering glass developed in 1851 that revived the race for large instruments. Easier to polish than a metal, of more stable dimensions, glass also had the advantage of being able to be stripped of a worn coating and resilvered without great difficulty. With their young but already powerful glass industry, the Americans proceeded rapidly toward very large instruments. In 1917, the Mount Wilson Observatory (California) received from Corning a 2.54 m mirror with which Edwin Hubble (1889–1953) explored the galaxies and discovered the expansion of the universe. Soon after, Pyrex (Chapter 7.6) made it possible to cast in 1934 for the observatory of Mount Palomar (California) a mirror of 5.10 m in diameter and 0.66 m in thickness, which took nearly a year to cool before being polished with a precision in the micron range. It weighs “only” 18 tons (instead of 30) thanks to a honeycomb structure that optimizes weight and rigidity. Until the manufacture in 1976 of the 6-m mirror of the Russian observatory of Mount Pastoukhov (Caucasus), it remained the largest glass piece ever cast.

3 The Enabler of Chemistry

3.1 An Alchemical Tradition

As a technical material, glass was also early put to use along with metal parts in various devices designed by Greek inventors [5], for instance, by Philo of Byzantium (fl. 247 BCE) with his “beautiful and enjoyable vessel” in the form of a “horn with glass hat for filling, siphoning and emptying actions” [32]. In his own *Pneumatics* [33], Hero of Alexandria (first century CE) later followed suit with the variety of his automata and recreational devices that were relying on the force of water vapor and air (Figure 8).

From a more fundamental standpoint, glass represented a dramatic transformation of humble earths into wonderful substances akin to gems (Chapter 10.11). Its fusibility placed it in the same category as the metals then known. It thus attracted the alchemists' interest as a model substance to explain a variety of phenomena related to the philosophy of matter (Chapter 10.4, [34]). It was at the same time playing a great role in practical operations as a substance inert to acids, insensitive to flame, which neither allied nor corroded, and especially allowed the mysterious transformations of matter to be observed visually.

Throughout the four operations of the *Great Work* – decomposition, washing, reduction, and fixation – glass was ready to serve by its plasticity that predisposed its uses in vessels of any shapes (Figure 9). The still, which, for instance, led to the discovery of alcohol, was called the *philosopher's glass*, whereas the crystal-clear

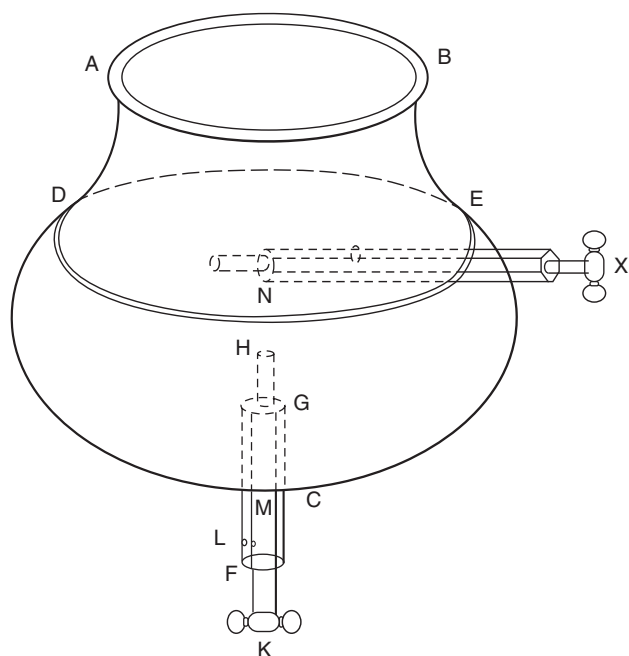


Figure 8 “A Cupping-Glass, to which is attached an Air-exhausted Compartment”: a piece of glassware described in the *Pneumatics* of Hero of Alexandria, section 56 [33].

philosophical egg was a large egg-shaped vessel in which the desired transmutation of base metals into silver or gold was expected to take place, under the right heat conditions, in contact with the mysterious philosopher’s stone. This stone had an incarnate red or ruby color, akin to those conferred to glass by copper and gold (Chapter 6.2). When they actually produced a red copper oxide, alchemists thus believed they had obtained the principle from which gold formed, hence the importance of copper calcinations described in the alchemical literature to prepare red glasses.

Alchemy was then eagerly practiced and developed further in Islam where the idea came that even living beings could be generated in glass vessels. To give a single example, the *Arabic Book of the Cow*, unduly assigned to Plato (~428–347), described the following *experiment* [37]:

For making deadly green scorpions. One should fast for one day, and at the end of the day chew the leaves of wild basilic, bind what was chewed in a glass tube, seal its mouth, and hang it in a dark, damp room which sunlight never enters. After forty days green scorpions will be born in it which, if they sting a man, will kill him.

In the alchemical tradition, the starting material inserted in the glass tube was thus considered to be the semen of the male animal whereas the tube itself was the womb in which the embryo gestated. Such tales did find an audience in Europe when Latin translations of the Arabic literature made them known from the twelfth century. But

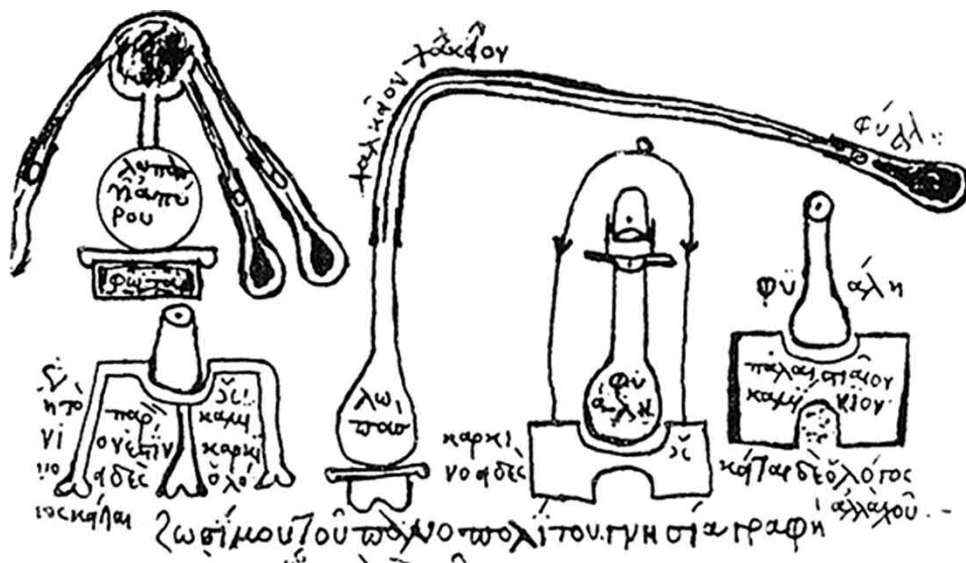


Figure 9 One of the earliest representations of alchemical glassware (MS 2327, BN Paris [35]): a thirteenth-century copy of a work by the Greek alchemist Zosimos of Panopolis (third to fourth centuries CE) [36]. From left to right: *tribicos* (top), jar on tripod (bottom), alembic, apparatus similar to a crab and phial on stove.

of more practical interest was then the *urinal*, a kind of glass beaker in which urine was carefully examined by the doctor who sought to find the secret of the patient's health in the turbidity and color of the humor.

Although attempts at making noble metals and animal generation were doomed to failure, the glass paraphernalia of the alchemist not only proved to be valuable when chemistry smoothly replaced alchemy, but was further augmented. To name a few items, the *retort*, *matras*, *cucurbit*, *beaker*, *coil*, *crystallizer*, *funnel*, *test tube*, *watch glass*, *cruet*, *syringe*, or *pipette* attest to this ever-increasing variety of glass chemical vessels (Figure 10). The reasons for this success were well known, explained the chemist and ceramist Pierre Joseph Maquer (1718–1884):

Good glass vessels should always be used in preference to all others, whenever possible, both because they do not give the most active solvents a hold, and do not allow anything they contain to leak out, and because they are transparent, they give the chemist the freedom to observe what is happening within them, which is always useful and interesting. [39]

3.2 The Last Blow to Aristotle's Natural Philosophy

In contrast to Aristotle's cosmology, which had suffered a fatal attack from the telescope, other points of the Aristotelian natural philosophy not only had not been challenged but been supported from experimental investigations made from the seventeenth century. This was the case of the mutual transformations of the four elements – fire, air, water, and earth – through exchange of their respective *qualities* (dry and hot for fire, wet and hot for air, wet and cold for water, and dry and cold for earth). As reviewed by Antoine-Laurent de Lavoisier (1743–1794) [40], distinguished investigators, for example, thought that the transformation of water into earth was demonstrated by the gain weight of plants grown in pots whose own weight did not change, as well as by the white, earthy powder always found in glass vessels after repeated water distillations. The eminent Robert Boyle (1627–1691) was one of the practicing chemists who stated that this *Terrestrial substance* recovered, even after distillation of rain water, led “to suppose the Transmutation itself to be real,” and to conclude that

if the purest Water may be turn'd into Earth, it will not be easie to make it improbable that the other Ingredients of mixt Bodies, which the Chymists call their Hypostatical Principles, are capable of being transmuted into one another. [40]

To Lavoisier, however, the transmutation of water into earth was just “a gratuitous assumption” [41], which he set to disprove with the help of his balance in a famous series of experiments. Of particular importance was the fact that, after repeated water distillations, the weight of the dried recovered deposit was the same as the weight loss of the glass vessel. Among other implications of his observations, Lavoisier concluded

that water does not change in any way in nature, & that it does not acquire any new properties by repeated distillation; [...] That the very substance of the glass itself is subject to solution in water; & that there is, as for all salts, a saturation point, beyond which no further solution can take place. [42]

In other words, the results reported by Boyle and other experimentalist during more than a century, “far from proving the possibility of changing water into earth, would rather lead them to believe that it is unalterable” [42]. At last, the postulate of the mutual transformations of the elements was thus ruled out for good after two millennia of acceptance.

3.3 An Ever-Increasing Usefulness

Ironically, glass had not served chemistry by its much vaunted inertness but by its alterability to ensure the demise of the last vestige of Aristotle's natural philosophy and, therefore, to pave the way to the new system of chemistry that would emerge at the end of the eighteenth century. Glass of course did not lose its privileged place along the way: without it, there would have been simply no chemistry and experimental biology would have also missed a key experimental component. Glass thus kept being strongly praised, as done by Jean-Baptiste Dumas (1800–1884), a pioneer in organic chemistry (and Pasteur's mentor), who stated in his *Treatise of Chemistry* that

what is really characterizing our modern civilization is its use by physicists and chemists in their experiments. An in-depth study of chemistry is not needed to acknowledge that it is thanks to glass that this discipline owes all its advances that have allowed its present theory to be established, so fertile in wonderful applications. [43]

In the same spirit, Dumas' friend Justus von Liebig (1803–1873) explained in his *Familiar Letters on Chemistry* that glass was a well-known and “curious substance” because of “its transparency, hardness, destitution of color, and stability under ordinary circumstances” [44].

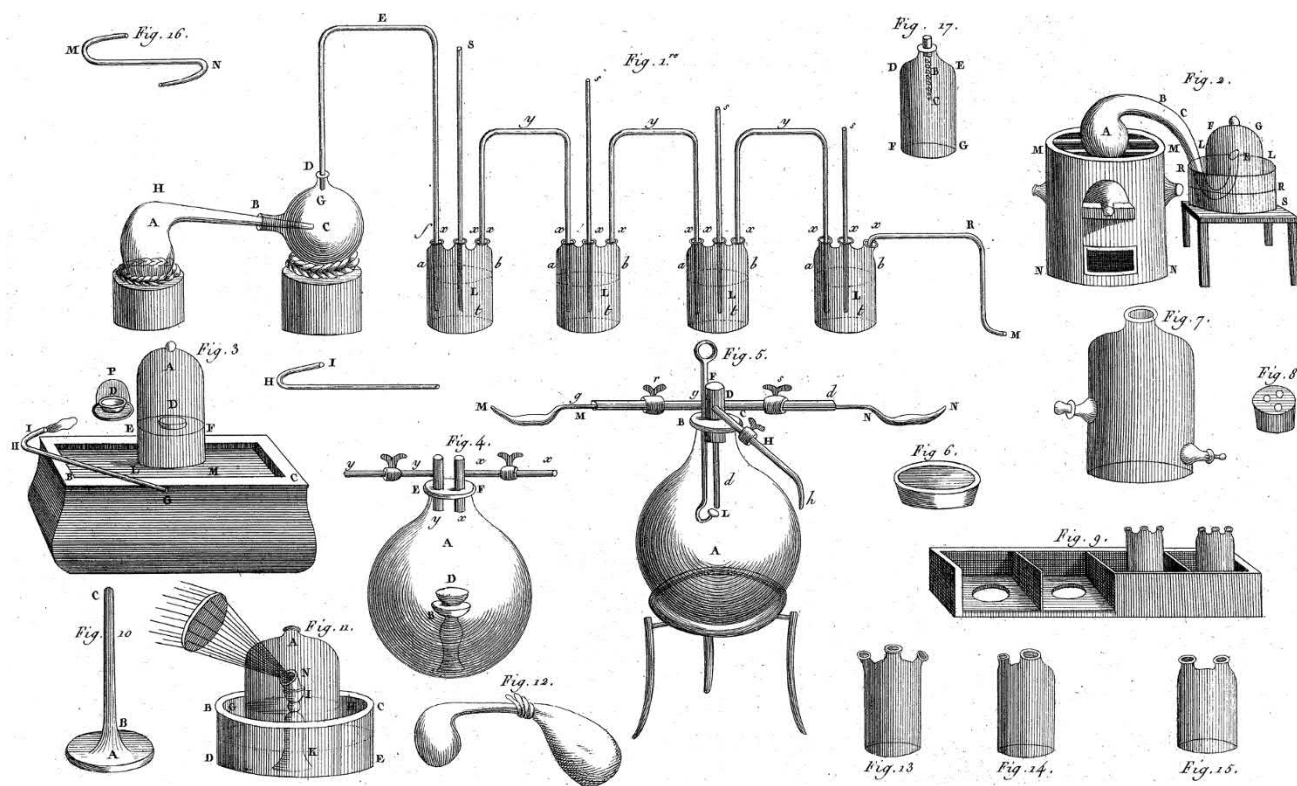


Figure 10 Lavoisier's chemical glassware at the end of the eighteenth century. Plate IV of his *Elements of Chemistry* [38], usually considered as the first modern chemistry treatise.

To these obvious qualities, he continued, we may add those “which especially adapt it to the use of the chemist,” namely, that it is unaffected by most acids or other fluids, becomes upon heating more ductile and plastic than wax to take the form required by every vessel and apparatus, and can be nicely combined with cork for connections. Chemical ware had then become made from *hard* Bohemian glass [45], a very homogenous material withstanding high temperatures and resistant to corrosion whose composition typically included 8 wt % CaO, 15% K₂O, and 75% SiO₂ (made from saccharoid limestone, tree ashes, and hyaline quartz mined in large veins). With his *Kaliapparat* made of five glass bulbs, Liebig himself pioneered determinations of the carbon, oxygen, and hydrogen contents of organic substances [45].

This importance of glass was even accrued in the early nineteenth century when glass tubes proved to be valuable vessels for electrolysis experiments thanks to their electrical insulating properties and transparency, which allowed electrode phenomena to be observed directly. The discoveries of alkali and alkaline earth elements (Chapter 10.11) are other examples of the chemical advances made possible by glass in electrical studies. At the same period, chemists began to be trained to blow themselves their glassware. The time of Lavoisier was thus over where “the rich alone could make chemical researches,” noted Liebig, because “the necessary apparatus could only be procured at a very great expense” [44]. Following him, chemists as famous as Jacob Berzelius (1778–1849) or Michael Faraday (1791–1867) also became expert glass blowers in a new tradition that would still be followed by PhD students in many chemistry departments as late as in the 1950s.

At the end of the nineteenth century, another important advance was made through the availability of silica glass (Chapter 10.11), which could be shaped at the very high temperatures required thanks to the new oxy-gas blow-torch [46]. Shortly afterward, the invention of borosilicate glasses (Chapter 7.6) finally provided chemists with ware more resistant to both leaching and thermal shock. In spite of the modern use of disposable (glassy) plasticware (Chapters 8.7 and 8.8), it should thus come as no surprise that inorganic glass is still and will long remain ubiquitous in chemical activities where it has actually found various new uses. Thanks to its lack of absorption bands in the relevant frequency ranges, silica glass has, for instance, become an indispensable auxiliary for a wide range of spectroscopy techniques (Chapter 5.1) in the form of cells and cuvettes for analyses of gases and liquids.

4 Hotness and Air Weight Measured

4.1 Temperature: The Thermometer

The notions of *temperature* and *heat* have remained entangled until the end of the eighteenth century. The eminent naturalist Lazzaro Spallanzani (1729–1799), for instance, believed that over long-enough periods of time, the fire of furnaces would reach an intensity sufficient to melt lava [47]. In thermodynamic terms, the difficulty was of course to distinguish intensive (temperature) and extensive (heat) properties. In a qualitative manner, the former was easiest to define. Dilation of air enclosed in a warm vessel had, for instance, been noticed in Antiquity by Philo of Byzantium or Hero of Alexandria. In a variety of the ingenious or recreational devices actually built described in their *Pneumatics* [32, 33], both of them also put to use the expanding and contracting powers of water upon vaporization and condensation, respectively.

But only toward the end of the sixteenth century was the dilation of air used in *thermoscopes* to measure temperature variations. Galileo himself designed such an instrument made up of a glass bulb, filled with air, and welded to a vertical capillary, filled with wine, immersed at its bottom in a cup of the same liquid. When becoming warmer, the air was displacing the wine meniscus whose position was determined by the temperature increase. For obvious reading reasons, glass was the only transparent material with which the apparatus could be built.

Not only was such a measurement of the degrees of heat or cold relative, however, but it was also sensitive to atmospheric pressure (still unknown at that time). More reliable instruments were thus designed when the first *thermometers* built in the early 1640s in Italy relied on the dilation of water or spirit of wine in glass [23]. Under the auspices of the *Accademia del Cimento* founded in 1657 in Florence by the Great Duke Ferdinand II of Tuscany (1610–1670), many kinds of devices were soon after designed with either vertical capillaries or coils (Figure 11). Important problems were then intercalibration of the instruments and the establishment of temperature scales to which Daniel Fahrenheit (1686–1736), René-Antoine Ferchault de Réaumur (1683–1757), Anders Celsius (1701–1744), and Antoine Baumé (1728–1808) would attach their names.

4.2 Air Pressure: The End of Horror Vacui

At the beginning of the seventeenth century, it was curiously observed in Tuscany that any siphon (or suction



Figure 11 The diversity and Venetian style of the vertical and spiral glass thermometers designed in Florence in the seventeenth century. Photo Franca Principe, Museo Galileo, Florence, inv. 20477.

pump) empties itself when the height of the water column exceeds about 18 braccia (10 m). The physicist Giovanni Battista Baliani (1582–1666) understood this effect as the result of the gravity of the air becoming insufficient to compensate the weight of water at both ends of the siphon. To check experimentally this conjecture, the mathematician Evangelista Torricelli (1607–1648) had the idea of taking a straight tube as the simplest form of siphon. To make direct observations possible, he turned to glass tubes filled with liquids denser than water, namely, sea water, honey, and finally mercury. When a tube filled with mercury, closed at one end, was immersed into a tub of the same metal at its other end, Torricelli indeed observed that the level of mercury was higher than in the tub. But was the empty space left at the top of the tube filled with mercury spirits or imperceptibly rarefied air? Repeating his experiment with devices of different lengths, inclinations and shapes, Torricelli found that the mercury was in each case rising to the same height (Figure 12). In two letters sent in 1644 to a friend to describe his experiments [49], he thus concluded that the force raising the mercury was external to the tube. As postulated by Baliani, therefore, this force originated



Figure 12 The pressure exerted by the atmosphere as indicated by the same height of mercury in glass tubes of different sizes, shapes, and inclinations partially immersed in a mercury tank. Engraving from [48].

in the gravity of the air and Torricelli also thought that it was changing because the air was “at times heavier and thicker and at times lighter and more rarefied.”

Torricelli's letters were widely circulated. Attempts were, for instance, made at duplicating his experiments in Paris, but the glass tubes drawn there did not resist the pressure exerted by 3 ft of mercury because their quality did not match that of those made by the Venetians working in Florence. Until the nineteenth century, tubes of large and small sections would be drawn from slightly cooled and very hot glass, respectively. In both cases, the blower shaped a gob in the form of a cylinder on which an aid stuck another gob. When the two workers moved evenly away from each other, the tube began by the blower lengthened regularly by taking glass from the gob carried by the aid while a third worker held a fan to cool down the tube where the desired diameter was achieved (Figure 13). Compared with the ware used in chemistry, the long glass tubes needed for quantitative experiments thus raised difficult technical problems to be straight and of uniform section and mechanically strong enough for not shattering under the weight of mercury.

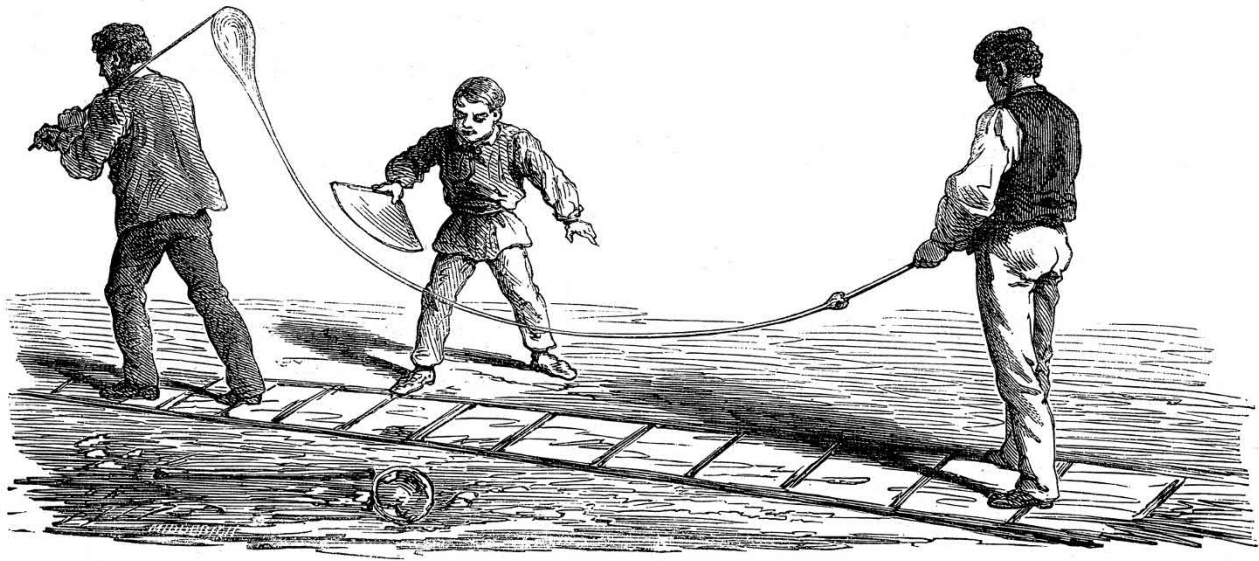


Figure 13 The traditional procedure for drawing glass tubes from two different gobs [31], which could be as long as 100 m.

Thanks to the better quality of Norman glass tubes, it was in Rouen that Torricelli's observation could be repeated in France on October 1646 by a team that included the young Blaise Pascal (1623–1662) and his father. To demonstrate the existence of vacuum, Pascal then performed experiments with a variety of devices, including glass tubes up to 50 ft long. Part of them were probably *thought experiments*, but a particularly significant result actually obtained was that of the “vacuum into vacuum” check whereby the mercury of a glass tube placed in a vacuum did not rise at all.

In the excitement generated by Torricelli, similar experiments had been made elsewhere. But Pascal was the one who made the most of them, first in a short letter [50] and then through the observations performed at his request in 1648 of the decrease of the height of mercury in a glass tube carried from the city of Clermont-Ferrand (elevation 358 m) to the top of the nearby Puy de Dôme (1465 m) while another tube was left in town to allow possible fluctuations in air gravity to be detected during the experiment. “It is quite certain that there is much more air that presses on the foot of the mountain than there is on its summit,” remarked Pascal [51]. And since “one cannot well say that nature abhors a vacuum more at the foot of the mountain than at its summit,” Pascal concluded that the observed variations definitely ruled out the antique *horror vacui*: “the weight of the mass of air is the true cause of all the effects hitherto ascribed to that imaginary state” [52]. Thereafter, the *continuous experiment* made from 1649 to 1651 at Pascal's request constituted the very first series of barometric observations,

which signaled the beginnings of meteorology in the modern sense of the term.

Pascal did not stop at this point. As he stated early [50], the effects caused by gravity and air *pressure*, a term that was for the first time used in its modern sense, illustrated the direct link between the study of vacuum and the new science of *hydrostatics* that was emerging with his *Treatise on the Equilibrium of Liquids* [52], completed in 1654 but published posthumously in 1663. Because of the principle that “liquids weigh in proportion of their height,” Pascal invented along the way the hydraulic press to intensify forces very simply (Figure 14). He also drew a number of consequences of this principle. It was, for instance, the *hydrostatic* nature of pressure in a liquid that made aquatic animals equally pressed on all sides and, thus, not feeling the weight of water. Among other things, Pascal could in addition estimate the weight of the whole atmosphere because the air at sea level was weighing as much as water 31 ft and 2 in. high. With some assumptions to account for the decreasing density of the air with increasing elevation, his result of 8.285×10^{18} pounds – derived from the height of mercury in a glass tube – was an impressive first step toward today's value of 10.48×10^{18} pounds (1 pound = 0.49 kg) [52]!

4.3 The Springiness of the Air

Since vacuum did exist, investigators rushed to study its most varied effects. Torricelli had himself tried to check whether bugs survived in a vacuum, but the mercury of

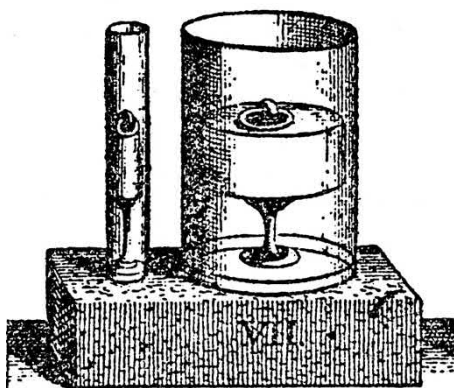


Figure 14 Pascal's hydraulic press [52], "a vessel full of water, sealed on all sides and provided with two apertures, one of them one hundred times as large as the other. If a perfectly fitting piston is adjusted to each, one man pressing on the smaller piston will exert a force equal to that of one hundred men pressing on the larger, and will exceed that of ninety-nine men doing the same. And whatever the relative areas of these apertures, if the forces exerted upon the pistons are in the same ratio as the areas, they will balance one another. Whence it follows that a vessel filled with water is a new mechanical principle and a new machine that will multiply forces to any amount desired; for a man by this means will be enabled to lift any weight that another may propose."

his glass tubes killed them too rapidly. Thanks to their tightness to air and transparency, glass vessels were of course the ideal complements of the vacuum pumps. These were designed with much inventiveness [23], in particular by Hooke when he was an assistant to Boyle. It was with Hooke's pump that Boyle observed in glass

vessels the elusive effects of a good vacuum: sound is, for example, no longer propagating, water is boiling at room temperature, whereas life and flame badly require air to be sustained [53].

Already in Antiquity the rebound of inflated balls had shown that air is an elastic body with a strength that, contrary to that of a spring, does not weaken. Again assisted by Hooke, Boyle studied this elastic force (the *springiness*) by measuring the volume of the air enclosed in a U-shaped glass tube when pressure was slowly increased through small mercury additions. From his results, Boyle concluded only in the second edition of the book [53] where his measurements were reported that "common air, when reduced to half its wonted extent, obtained near about twice as forcible a spring as it had before," and so on (Figure 15). While further work was done to check whether this law remained valid at higher pressures, as guessed by Boyle, the physicist Guillaume Amontons (1663–1705) investigated the effects of temperature on gas pressure [54]. Better known for the laws of friction he established, Amontons was also one of the first theoreticians of heat engines. His measurements indicated that Boyle's law was valid only at constant temperature as "unequal masses of air increase almost equally the force of their air spring by the same amount of heat." On this basis, Amontons invented the first gas thermometer and foresaw the intensive nature of temperature by noting "that unequal masses of air acquire equal spring forces by the same degree of heat."

But the remarkably fruitful physical career of mercury glass tubes was not over yet. Boiler explosions became increasingly frequent with the empirical development

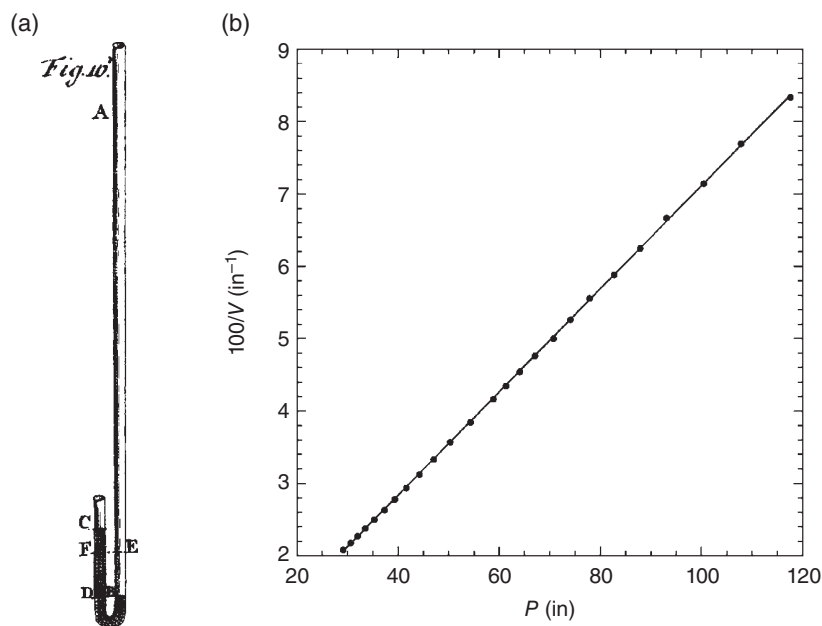


Figure 15 Boyle's mercurial experiments as made with "a long glass-tube, which by a dexterous hand and the help of lamp was in such manner crooked at the bottom, that the part turned up was almost parallel to the rest of the tube" [53]. (a) Tube of maximum length of 6 ft (1.8 m). (b) Constancy of the product of pressure (P) and volume (V) as represented anachronistically by a $P - 1/V$ plot (P and V expressed in inches of mercury in glass tubes; 1 in. = 2.54 cm), the remarkably small scatter in the data pointing to tubes of uniform enough sections.

of the high-pressure steam engine at the beginning of the nineteenth century. To impose safety precautions to these machines, the French government asked in 1823 the Académie des sciences for means of preventing accidental loss in men and property. Led by Pierre-Louis Dulong (1785–1838) and François Arago (1786–1853), a committee determined that the main risk originated in the lack of proper safety valves because the vapor pressure of water was not known under the relevant conditions. As they stated, “no physicist had hitherto dared to make experiments at pressures higher than 8 atmospheres because of the extreme difficulty of these kinds of research, and of the danger that accompanies them” [55].

Willing to perform measurements as accurate as possible, the Paris Academicians relied on the most difficult, but “most exact method,” namely, the direct measurement “of the mercury column able to equilibrate the elasticity of the vapor” up to 30 atm. For this purpose, glass tubes 2 m in length and 5 mm in diameter were assembled over a 20–25 m height to serve for measurements eventually performed up to 224 °C and 24 atm only because of boiler leaks at higher pressures. After having tried various empirical relationships, the Academicians fitted an equation to their results that later proved accurate up to more than 100 atm (Figure 16). In a sibylline way, they concluded that

only people accustomed to great experiments in physics can appreciate the enormity of the task that was imposed upon us, to which nothing comparable would be found in our records, and which necessitated on our part a dedication that the Academy perhaps had not the right to require from any of its members.

4.4 Sap and Blood Barometry

Even biology did not escape mercury glass barometry. It was a disciple of Newton, the Reverend Stephen Hales (1677–1761), who pioneered such measurements to determine the physical principles of the circulation of sap, in plants, and blood, in animals. In 1727, he described in his *Vegetable Statics* [56] how to measure the rise of sap as a function of season and time of day (Figure 17). A good century after the discovery of blood circulation by William Harvey (1578–1657), Hales then reported in 1733 in his *Hæmastatics* the research begun in 1706 on blood pressure [57], which he had long interrupted out of disgust for cruel experiments. His main aim was to discover “whether the blood, by its mere hydraulic energy, could have a sufficient force, by dilating the fibres of the acting muscles, and therefore shortening their lengths, to produce the great effects of muscular motion.”

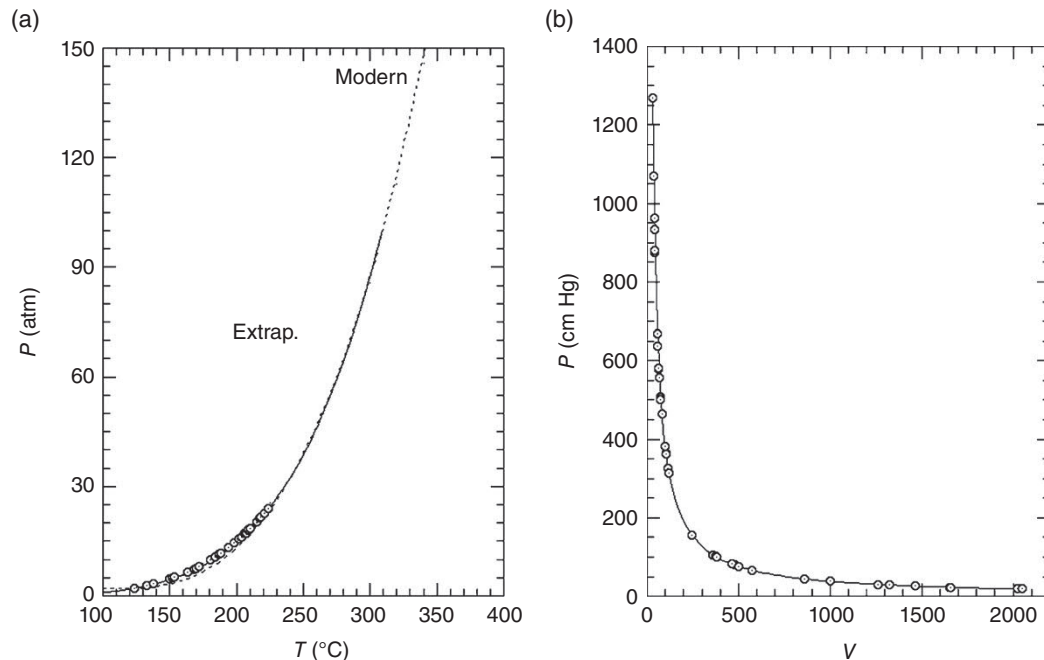


Figure 16 The key to the safety valve of steam engines [55]. (a) The vapor pressure of water as a function of mercury pressure in glass tubes; Eq. $T(^{\circ}\text{C}) = (P^{0.2} - 1)/0.7153$ fitted to the data. (b) The pressure–volume relationship of the vapor along this curve.

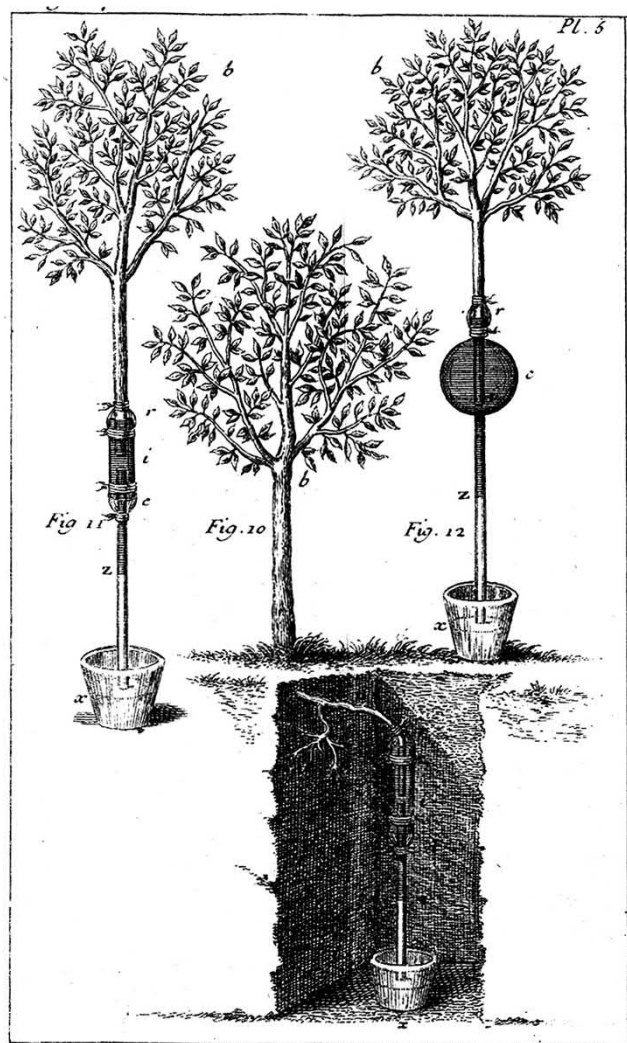


Figure 17 Pressure as a probe of the physiology of plants in experiments made by S. Hales to determine barometric depressions in vascular plants [56]. Ascent (z) of the mercury contained in tubes resulting from the absorption of the water filling the glass vases tightly attached to the root of a pear tree (Figure 10), the stem of a young apple tree (Figure 11) and the branch of a vigorous apple tree (Figure 12).

Hales, for example, measured the pressure in the crural artery of a mare, immobilized on her side, in which a 9-ft (2.7 m) long glass tube filled with mercury was implanted through a brass pipe.

In further measurements, Hales observed that blood pressure is much lower in veins than in arteries, that it is characteristic of every species (dog, ox, sheep, fallow deer) and, in addition, that it probes the cardiac condition of an animal. But this force of arterial blood in capillaries was far too low to cause muscle contraction, concluded Hales who suggested with insight that “this hitherto inexplicable Mystery of Nature must therefore be owing to

some more vigorous and active energy, whose force is regulated by the nerves” through electrical effects. The relevance of electricity to neuromuscular processes was thus surmised by Hales, who pointed out that an electrical virtue could indeed be conveyed over great length even through a human body.

5 From Electrostatics to Subatomic Physics

5.1 The Beginnings of Electrostatics

In the burst of scientific activity of the early eighteenth century, much attention was actually paid to electric phenomena, which were clearly representing a *terra* still largely *incognita* that it was now time to explore. These phenomena had been termed *electric* by the physician William Gilbert (1544–1603) because of the curious power acquired upon rubbing by amber (*elektron* in Greek, *electrum* in Latin) to attract light objects, which had already been known in Antiquity. By a twist of history, glass tubes were at the roots of a renewed interest in these phenomena. The astronomer and priest Jean Picard (1620–1682) had already noticed the light emitted in a vacuum at the top of a mercurial tube jostled in the dark, but a really strong interest in the phenomenon arose only after Francis Hauksbee (~1660–1713) [58] and Pierre Polinière (1671–1734) [59] independently reported in 1709 their experiments on the strong luminescence emitted by these tubes upon rubbing.

Confusion quickly resulted from the wealth of observations recorded when various kinds of materials were rubbed although an important distinction was made by the dyer Stephen Gray (1666–1736) who discovered that bodies were either conducting the *electric virtue* of a glass tube or not [60, 61]. Interestingly, glass again played a pivotal role in the clarification of this confusion in 1733. From well-designed series of experiments, the polymath Charles Du Fay (1698–1739) understood in 1733 that there are in fact two kinds of electricities [62, 63]. Creating a nomenclature that would hold until the end of the nineteenth century, he termed them *vitreous* (positive) and *resinous* (negative), not because they were yielded only by glass and copal (a kind of clear amber) but simply because he discovered them with these two substances. And Du Fay implicitly made use of the philosophical *Principle of sufficient reason* to add: “If there are in nature only these two kinds of electricity, which seems quite likely to me, because one attracts what the other repels, I don’t really imagine what effect a third one could have” so that all bodies, “with the exception of metals, will be in one or the other of these two classes” [62].

It would take a long time to understand that glasses are *dielectrics* (another term coined by W. Whevell), i.e. they are polarizable electrical insulators. Without knowing it, mid-eighteenth-century *electricians* thus took advantage of this feature in two important devices. One was the *Leyden jar*, the first capacitor made up of two metal foils cemented inside and outside a glass jar with which voltages of up to 60 kV could be reached by friction, and which made controlled accumulation and discharge of electricity possible. The other was the electrostatic machine (Figure 18) with which voltages of up to 330 kV were obtained at the end of eighteenth century. These machines came in many kinds [65] although they all involved rubbing of glass in the form of globes, cylinders, or disks whose largest diameter of 1.65 m eventually reached what was in fact the size limit achievable with the crown process (Chapter 10.8). Especially with the electrostatic machine, all effects that could be imagined were studied, raising considerable interest in the public because of the spectacular features observed (Figure 18), in particular when the electrical conduction of the human body was put into play to produce sparks or let participants feel the delicious thrill of discharges.

5.2 The Womb of Subatomic Physics

Following the invention of the electrical pile by Alessandro Volta (1745–1827) in 1800 and the discovery of the interaction between electricity and magnetism by Hans Christian Ørsted (1777–1851) in 1820, the physicists' interest shifted to the new field of electromagnetism to which metal conductors, and not glass vessels, were actually relevant. But glass did come back to the fore in the second part of the nineteenth century after improvements in mercury pumps had made it possible to reduce further the pressures obtained in evacuated tubes. Of particular interest was the electrical conduction in rarefied gases in relation to the properties of *ether*, the elusive fluid filling all space whose existence was postulated for the propagation of electromagnetic waves. According to some physicists, for example, a complete vacuum should have been a perfect electrical conductor since the lack of any matter would have allowed the ether to flow without any resistance.

In view of the importance of the problem, much effort was made, in particular by the physicist and glass blower Henrich Geissler (1814–1879), to improve *discharge*

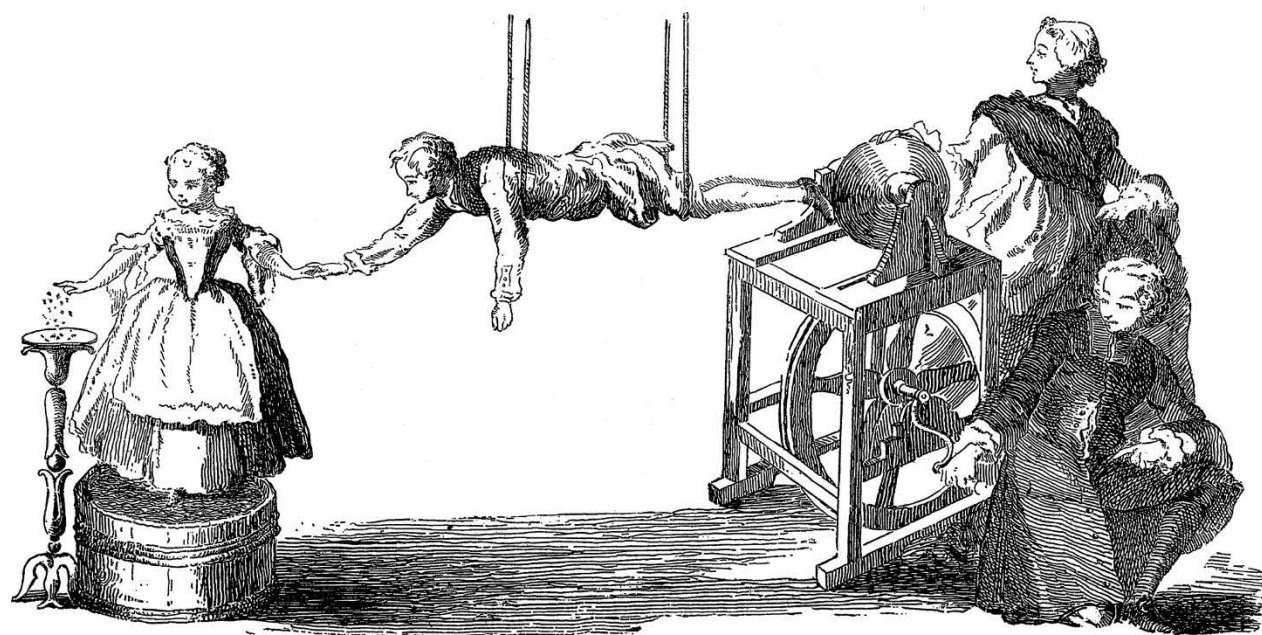


Figure 18 A typical eighteenth-century electrostatic experiment made by Christian August Hausen (1693–1743) at Leipzig [64]: *vitreous* electricity produced by the lady's hand rubbing the rotating glass disk, transmitted from the shoe to the arm of the fellow (suspended by insulating silk threads to the ceiling, as pioneered by S. Gray [60]), and finally to the girl who is attracting small gold leaves with her hand, adumbrating in this way the electroscope. While the girl is standing up on an isolated pad, the lady carries off with her body the *resinous* electricity to the ground. The involvement of these two women and of the churchman, who is turning the crank of the electrostatic machine, illustrates the wide interest of the public at large of the period in such experiments.

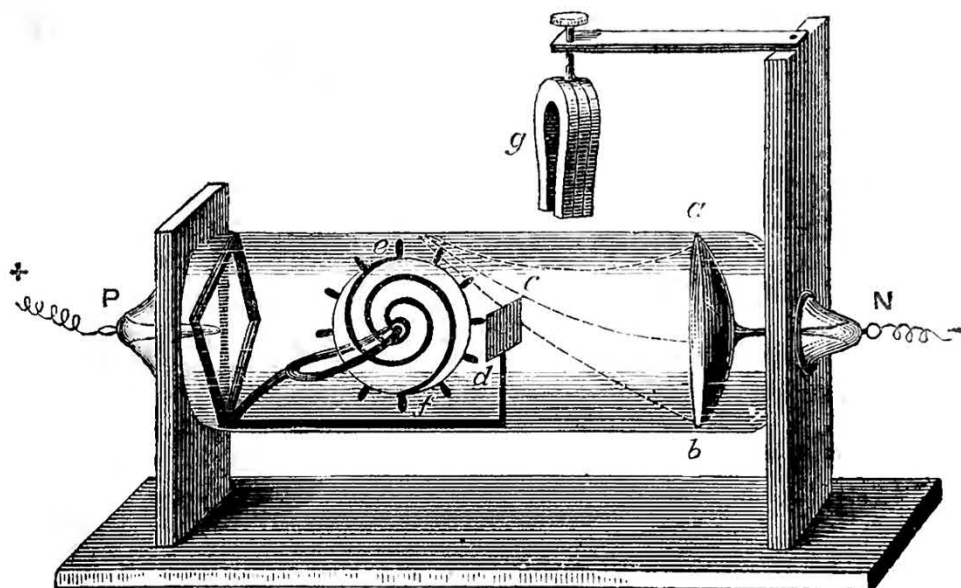


Figure 19 The good use by Crookes of transparency and other properties of glass: the observed rotation of a mica toothed wheel (*ef*) when the rays emitted by a cup-shaped cathode (*ab*) toward an absorbing mica plate (*cd*) are deviated upward by the field of a magnet (*g*) [67].

tubes, i.e. evacuated glass tubes through which two electrodes are welded (the ancestors of the neon lighting tube, see Chapter 6.9). When a voltage was applied, electrical transport was signaled by a bluish glimmer extending from one electrode to the other accompanied by a greenish light appearing at the end of the tube opposite from the cathode. This emission was thus termed *cathode rays* (cf. [66] for a detailed account). An important step toward understanding their nature was made when, taking advantage of the pressures as low as 10^{-6} atm he could reach, the physicist William Crookes (1832–1919) designed a variety of experiments thanks to which he observed that these rays are emitted perpendicularly to the cathode, are deviated by a magnetic field (Figure 19), induce a strong luminescence when impacting the opposite side of the tube, and especially that a metal leaf placed along their path produces a shadow of the same form (Chapter 6.10, Figure 3). Crookes thus suggested in an 1879 lecture that a new type of corpuscular radiation could exist independently of electromagnetic waves [67].

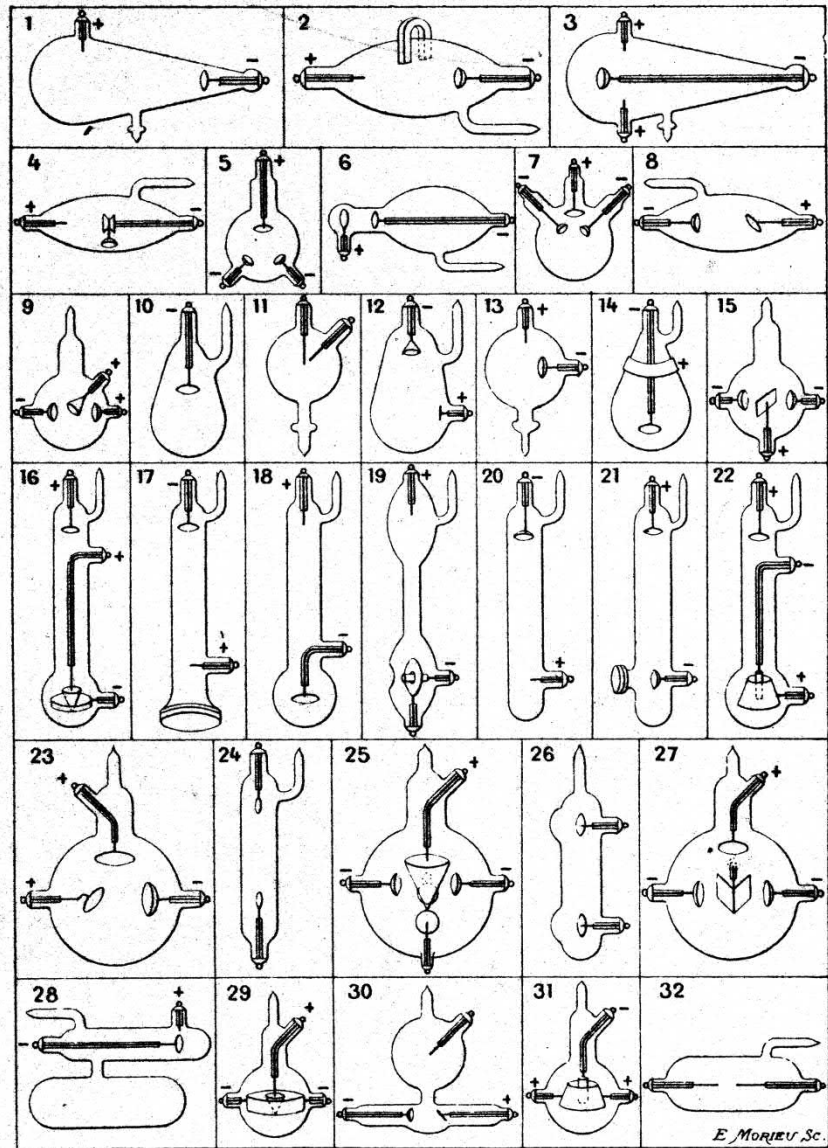
Further work showed that these rays impress photographic plates and carry negative electric charges. When investigating them, the physicist Wilhelm Röntgen (1845–1923) noticed that an external fluorescent screen placed at some distance from the tube emits a luminescence whose intensity increases if brought closer to the tube. When putting his hand between the tube and the screen, Röntgen had then the striking surprise to see his own bones. He had discovered a new kind of radiation [68], which would be termed X-rays because of their

enigmatic nature. This strange radiation indeed traversed glass tubes but did not undergo refraction nor was deflected by a magnetic field although, as Röntgen also showed, it was partially absorbed by all substances in varying degrees. The impact of this discovery was so strong, even on the general public, that glass tubes of any shape were designed to investigate further X-rays and their most various physical, chemical, and biological effects (Figure 20).

But the cathode rays themselves were remaining enigmatic. In Cambridge, measurements of their deflection by electric fields by the physicist Joseph J. Thomson (1856–1940) indicated that they involve particles lighter than atoms. By deflecting the rays in a glass tube with both electric and magnetic fields (Figure 21), Thomson then determined the ratio of their charge and mass and, in 1899, these two parameters separately [71]. Interestingly, these negatively charged corpuscles were the same regardless of the metal of the cathode and their mass was 2000 times smaller than that of the lightest ion, hydrogen. Thanks to ever higher vacua that allowed electrons to travel without undergoing collisions along their path, a dogma had collapsed: the atom was not the smallest unit of matter. These corpuscles took on the name earlier proposed in 1891 by George Stoney (1826–1911) for the fundamental unit of electric charge, the *electron* [72].

In his 1879 lecture, Crookes had said that “in studying this fourth state of matter we seem at length to have within our grasp and obedient to our control the little

Figure 20 The great many types of X-ray tubes designed during the year 1896 alone [69].



N^o 1 à 32. — Divers modèles d'ampoules pour radiographie et fluoroscopie. — N^o 1 et 2. Ampoules de Crookes. — N^o 3. Ampoule Séguy. — N^o 4. Ampoule Wood. — N^o 5. Ampoule Séguy. — N^o 6. Ampoule Chabaud et Hurmuzescu. — N^o 7. Ampoule Séguy. — N^o 8. Ampoule Thompson. — N^o 9. Ampoule Séguy. — N^o 10. Ampoule d'Arsonval. — N^o 11. Ampoule Séguy. — N^o 12. Ampoule Puluj. — N^o 13. Ampoule Séguy. — N^o 14. Ampoule d'Arsonval. — N^o 15. Ampoule Le Roux. — N^o 16, 17 et 18. Ampoules Séguy. — N^o 19. Ampoule de Ruz. — N^o 20. Ampoule Crookes. — N^o 21, 22, et 23. Ampoules Séguy. — N^o 24. Ampoule Röntgen. — N^o 25. Ampoule Brunet-Séguy. — N^o 26, 27. Ampoules Le Roux. — N^o 28. Ampoule Colardeau. — N^o 29. Ampoule Séguy. — N^o 30. Ampoule Colardeau. — N^o 31. Ampoule Séguy. — N^o 32. Ampoule Röntgen.

indivisible particles which with good warrant we suppose to constitute the physical basis of the universe" [67]. Crookes' intuition was thus vindicated by Thomson. When combined with transparency, tightness to gas and shapability, the high electrical resistivity, weldability

with metals, and penetrability by electric and magnetic fields of glass had surreptitiously led from electrical conduction in gases to subatomic physics. At last, the alchemists' picture of glass vessels as wombs for wonderful phenomena had come true in some unexpected ways!

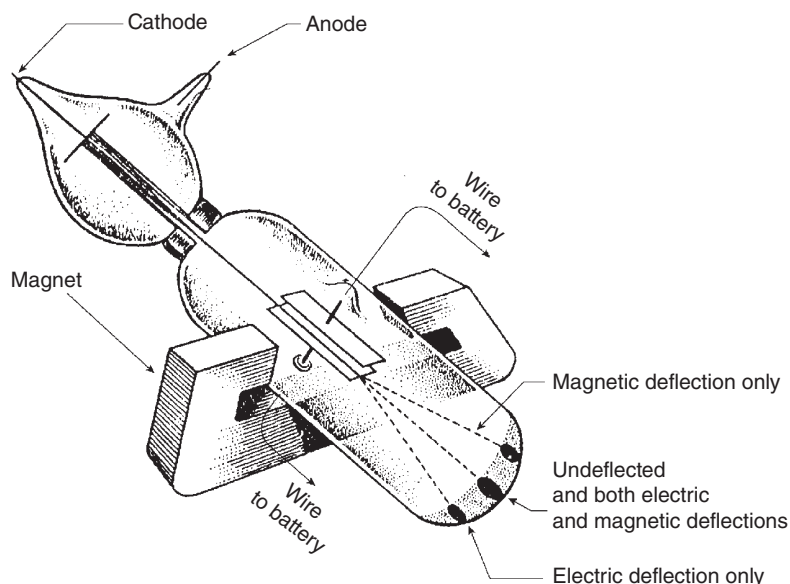


Figure 21 An important evolutionary step between discharge tubes and mass spectrometers: the glass device designed by J.J. Thomson for measuring the deflections of charged particles by electric and magnetic fields. Source: After [70].

6 Perspectives

Has it ever been estimated how much of the humanity's literary, artistic, or scientific achievements is indebted to two small pieces of glass resting on the nose and held to the ears by two temples? The answer would illustrate most simply the impact that glass have had upon man's activities throughout the ages. Regarding science, the most important conclusion to be drawn from this selective review is that, in none of its uses, glass could have been replaced by another material. The conclusion is anything but new. When celebrating glass in the flowery language of his time, the Russian polymath Mikhail Lomonosov (1711–1765), for example, marveled on the way in which studies of the discharge of electricity accumulated by friction on glass had given rise to the lightning rod:

Turning about, the Glass globe gives off blows with brilliance, resembling thunder and lightning with their crashing and glare", so that "the same power of roaring clouds which brings on darkness issues also from the movement of Glass! Knowing the laws discovered by Glass, we thus can turn lightning away from our dwelling places. [73]

Glass in fact nicely illustrates the statement often made that the history of science is largely that of scientific instruments thanks to whole new fields of inquiry repeatedly opened. Although only a few individuals could be mentioned within the scope of this chapter, the large numbers of people who collaborated or competed to integrate glass in these instruments is most simply attested to

by the variety of designs that appeared right after the invention the telescope, the microscope, or the discharge and X-ray tubes. In this respect, diversification in glass composition and improvements in glass making also played a major role as illustrated by flint glasses and the Guinand process whose benefits for astronomy were immediate (Figure 22).

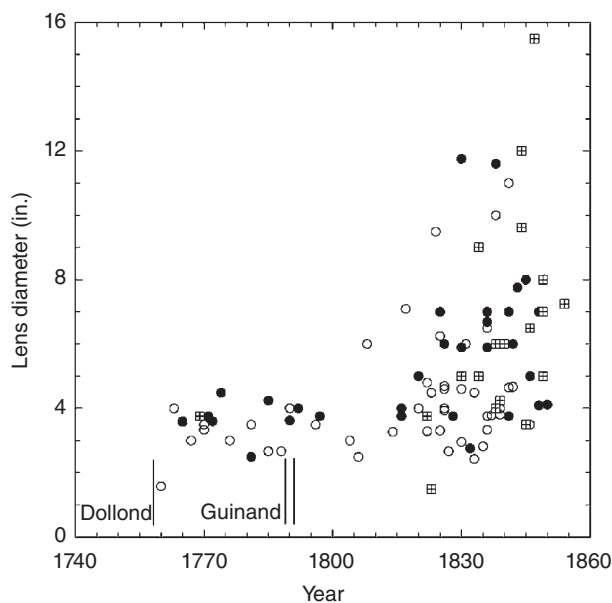


Figure 22 Glass technology in the service of astronomy: following Dollond's work, the introduction of achromatic lenses for refractors and the marked increase of their sizes then triggered by Guinand process. Open circles: continental Europe; solid circles: United Kingdom; crossed squares: rest of the world (mostly USA). Data from [74].

After a time lapse of a few centuries between the first practical applications of optics in spectacles – the earliest technological invention made in Occident – glass became the most powerful weapon against the Aristotelian worldview and its *horror vacui*. The purely qualitative nature of Aristotle's natural philosophy found in addition itself under attack since varying degrees of hotness became at last distinguishable at the same time that pressure was defined and measured. In Leeuwenhoek's expert hands, a tiny globule of glass became shortly after what has probably been the simplest scientific instrument ever designed with which epochal observations were nonetheless performed. Although barely more complicated, the mercury glass tube also lent itself to ground-breaking observations; with Pascal's hydraulic press, it even gave rise to one of the very first practical applications directly derived from scientific theory in modern times.

Following the initial outburst of the revolutionary seventeenth century, advances might seem to have slowed down afterward. The actual picture is more subtle, however, as new fields of research continuously emerged as a result of further technological progress. It was, for instance, only at the beginning of the nineteenth century that the small lenses of the compound microscope could be made achromatic [5]. Histology or microbiology – and its considerable impact on medicine through the discovery of pathogen microbes – then benefitted much from the ensuing sharper images and higher magnifications.

Likewise, a rigorous science of rocks came on the scene in the 1850s once the discovery of the polarization of light made it possible to identify rock-forming minerals from their specific dichroism. The first advances were made by William Nicol (1768–1851) who designed calcite (CaCO_3) prisms with which light could be conveniently polarized in a known direction of the microscope [75]. Nicol then had the idea to observe opaque rocks in very thin, and thus translucent, sections glued on glass slides and protected by glass coverslips. Slightly later, however, it was Henry Clifton Sorby (1826–1908) who fully realized the potential of the technique. He thus really launched the new science of *petrography* thanks to the possibility of identifying minerals and characterizing their mutual relationships in a given rock [76].

Such observations were soon to play also a fundamental role in glass science in conjunction with the quenching method [77] to determine most phase diagrams of interest from simple to complex systems (Chapter 10.11). The liquidus temperature is signaled by the appearance of tiny, generally birefringent crystals. Under the petrographic these crystals are in general readily detected in the glass groundmass of the quenched charge and, in solid

solutions, their optical properties may in addition allow their composition to be estimated. The solidus is in contrast characterized by the disappearance of the glass phase within a crystalline-phase assemblage, which is, however, more difficult to observe.

The antique glass vessels went themselves through completely new transformations that took implicitly advantage of the dielectric glass properties to become, for instance, large capacitors or discharge tubes. Although the relative permittivity of crown glass of about 5 is not outstandingly high, no other substance yield such a solid, isotropic, electrically insulating, mechanically strong, and readily shaped material. Since then, new ways to shape glass or modify its composition have resulted in other original advances. In this respect, a most important achievement has been the glass electrode for pH measurements, which combines physical and chemical effects so complex that they are still not fully understood (Chapter 5.8). As for optical fibers for the visible range (Chapter 6.4) or infrared optics (Chapter 6.5), their applications to chemical analyses, remote control, or communication technologies are too well known to be reviewed here, even briefly.

Finally, one should not overlook less visible but numerous applications of glass, for instance, in fibers (Chapter 1.6) reinforcing the printed-circuit boards that are nowadays ubiquitous in scientific computing and instrumentation. A quite different use is that of silica aerogel, which has proven valuable as a nonpolluting net to trap tiny extraterrestrial matter traveling in the solar system and bringing it back on Earth for study (Chapter 8.3). Thin films (Chapter 6.8) have also become highly relevant to scientific activity as recently illustrated by the detection of gravitational waves. With a modified Michelson interferometry, the sensitivity of the detectors has relied on silica glass mirrors coated with multi-layer thin films (Chapter 6.8) to reduce reflection losses to ppm levels. Such an appropriate reduction has been achieved with ion-beam sputtered multilayers of amorphous SiO_2 and TiO_2 -doped Ta_2O_5 [78]. From a thermodynamic standpoint, these materials are also of great interest because the structures of related SiO_2 - HfO_2 and SiO_2 - ZrO_2 coatings conform to simple predictions, which has suggested that “a transient, possibly liquid-like metastable state is reached during film formation” [79]. These coatings thus exemplify the never-ending adaptation of glass to new scientific enquiries, which is now taking advantage not only of hitherto unusual composition domains but also of new synthesis processes. Others will likely follow, a case in point being hybrid organic–inorganic amorphous materials whose original properties are now raising so much interest (Chapter 8.9).

Acknowledgments

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10.11

A History of Glass Science

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1 Introduction

What is glass? And what is peculiar to this form of matter to justify the existence of a specific *Glass science*? In a glass history that began about three millennia and a half ago, both questions have been making sense only in the last century. Whether glass would have been defined in terms of structure or of properties, experimental and theoretical means were of course lacking to arrive earlier at anything resembling modern standpoints. As a material, however, glass did not escape reflections from savants throughout the ages even though its making was remaining an empirical practice. The present contribution will try to make it clear for the five broad, overlapping periods that have been distinguished with the part of arbitrariness and lack of comprehensiveness inherent to short historical accounts. It will thus complement to the chapters devoted to early technology (Chapter 10.9) and to the scientific advances made possible by glass (Chapter 10.10).

Beginning in Antiquity, the first period lasted until the Middle Ages. The most obvious features of glass were its transparency or its vivid colors, which made it akin to gems, and its production from a melt, like that of metals. From the Near East to the Latin West, this dual kinship with precious stones and metals thus remained of particular concern during about two millennia. In the early modern period, glass became the subject of a different kind of rational enquiry. Experiments were made to understand some fundamental properties of matter at a time when the dramatic advances in the exploration of the universe made possible by glass lenses (Chapter 10.10)

led to the first speculations on the microscopic constitution of glass-forming liquids.

From the late eighteenth century, a few decades then heralded the entry into a scientific age in the modern sense of the term. This change was felt by the glassmakers of the period as illustrated in 1791 by the *Essay on the Art of Glassmaking* where the chemist Pierre Loysel (1751–1813) stated that

Glassmaking is, among all the arts, the one that can be rigorously submitted to the principles determined by physics, the one that, therefore, can reach the greatest precision, but it requested an observer who would be as familiar with all its processes as instructed in physics. [1]

In fact, it was not so much physics than chemistry that was about to influence glassmaking most as exemplified in 1810 by the *Attempt to Establish the Art of Glassmaking on Scientific Principles* authored by Aldolph Ferdinand Gehlen (1775–1815) who explained how Glauber's salt (sodium sulfate) could be used as a new source of soda [2, 3]. Until then, a glass could be basically characterized only by its density and index of refraction. Hence, the great novelty was the concept of *chemical composition* that resulted itself from the notion of *oxides*, which replaced that of *earths*, and the discovery of the relevant chemical *elements*. In parallel, a new attention was paid to the relationship of glasses with crystals, which made kinetics entering the picture of both glass formation and crystallization.

Following the first systematic measurements of physical properties, a specific *glass science* was finally born in the 1920s when consistent evidence pointed to the existence of a glass transition and experimental means became available to study disordered atomic structures. Since then, glass science has grown tremendously as is

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obvious to any reader of the *Encyclopedia* and summarized in an extensive bibliographic study [4]. Hence, this fifth and last period will not extend beyond the mid-twentieth century to avoid unnecessary overlap with other chapters. Owing to an apparent lack of any in-depth historical study of Glass science in the literature, this chapter will nonetheless be longer than others and its bibliography more detailed, as it must be in any such account. In preamble, however, it may be useful to review briefly how the definition of glass has evolved in response to the advances made in the understanding of this material, which is now termed *structural* glass to distinguish it from the newer spin, orientational or vortex glasses.

2 Glass: An Impossible Definition?

Traditionally, glass was defined by the manner in which it was made. It “is a more or less transparent material, coloured or colourless, shiny, fragile, smooth in its fracture, & which is produced by the fusion of vitrifiable stones or earths from saline, alkaline & metallic lime substances” [5], asserted in 1774 Antoine Baumé (1728–1808), best known for his work on thermometer intercalibration and the invention of the *areometer* for measuring the densities of liquids. Half a century later, the chemist Louis Jacques Thénard (1777–1857) stated more simply in an influential treatise that “Glass is a product one obtains by exposing a mixture of silica and different substances, most of the time very fusible, to the action of a violent and sufficiently continuous fire” [6].

These definitions could have already been given in Antiquity. Perhaps the most detailed one was that of Theophrastus (~371–287), Aristotle’s friend and successor as head of his school, the Lyceum. After having noted in his treatise devoted to stones that “earth indeed may undergo processes of melting, softening and hardening again,” Theophrastus added: “if, as some maintain, glass is made from vitreous earth, so too it is firing that causes this earth to become glass” [7]. As made by Jean-Baptiste Dumas (1800–1884) for sugar, sulfur, and arsenic oxide, however, other kinds of substances were already regarded in the nineteenth century as vitreous not from their chemical composition and mode of synthesis, but from their luster, translucency, shapability, or conchoidal fracture [8]. But chemistry was playing other tricks. From silica, silicon was first prepared in the form of a brownish powder by Thénard himself and Joseph Louis Gay-Lussac (1778–1850) through reaction of *siliceous hydrofluoric acid* (silicon tetrafluoride) on potassium [9]. But the two friends did not realize that they had isolated a new element and still less that it was in an amorphous state.

Considering such a new substance as vitreous would have thus led to abandon any convenient macroscopic criteria to characterize a glass. Selenium, which was discovered in 1818 by Jacob Berzelius (1779–1848) [10], was especially interesting in this respect because it existed as both an *amorphous* powder and a *vitreous* form, which were rapidly shown to be identical [11]. In addition, selenium had the original property observed in 1851 by Johann Wilhelm Hittorf (1824–1914) to “melt” without any heat effect [12], and was found in 1871 to be highly refractive and dispersive with an index of refraction varying from 2.65 to 2.98 [13], which illustrated considerable differences in physical properties with the traditional silicate glasses.

Alternatively, the need of annealing might have looked typical of glass. As explained by Baumé,

When the glass cools quickly, the two inner and outer surfaces of the pieces first take on all their strength, and then retreat: but the middle of its thickness is still red and soft; it is in a state of compression; it forms a spring that remains in a state of tension, and is always ready to break the obstacle that hampers it; this is what happens to all glass vessels that are a little thick, and have been badly annealed. [5]

Regardless of this particular interpretation, an “annealing” criterion to define glass would have been irrelevant anyway to amorphous substances not prepared in large pieces whereas the need of slow cooling was not unique to glass. It was also required for many ceramics as a result of the volume change at the α – β transition of quartz, which would be discovered only at the end of the nineteenth century by Henry Le Chatelier (1850–1936).

In a closely related modern variant, glass has been defined as a substance whose second-order thermodynamic properties (heat capacity, thermal expansion coefficient, and compressibility) vary abruptly in a narrow temperature interval upon heating. But this criterion is not generally valid since solid phases akin to glasses produced vapor deposition (Chapter 3.14), pressure-induced amorphization of crystals (Chapter 3.10), or sol–gel reactions between starting organic liquids (Chapter 8.2) may crystallize or decompose before undergoing a glass transition. As a matter of fact, even some silicate glasses quenchable at not extreme rates (e.g. Na_2SiO_3) crystallize rapidly hundreds of degrees below their estimated glass transition ranges.

Alternatively, glass has been defined in terms of structural disorder at the atomic scale, which is making sense in view of the tight connection between this disorder and typical macroscopic features of glass such as unlimited

shapability, lack of grain boundaries, mechanical strength, or extent of solid solutions. From a purely material standpoint, glass thus is commonly said to be a substance deprived of the long-range order of crystals. Because a good definition must be positive and not negative, however, one is then faced with the problem of stating the kind of order existing in glasses, which is known to lack a universal solution.

There nonetheless seems a possibility to conclude this discussion positively. Glasses are *solids*, i.e. substances whose atoms occupy essentially fixed positions. At any scale, they are *a-morphous* in the original sense of the term, which means that they are deprived of any characteristic shape. Compared with crystalline solids, they have in addition an original feature first reported for a variety of silicate glasses in 1845 by Eugène Chevandier (1810–1878) and Guillaume Wertheim (1815–1861), in the case of density and elasticity, which is that their properties differ depending on whether they are quenched or annealed [14, 15]. It is thus tempting to define very simply a glass as a macroscopically homogeneous amorphous solid whose properties (physical, chemical, or structural) vary with its preparation conditions; this definition in particular implies that internal thermodynamic equilibrium does not obtain since knowledge of two state variables such as temperature and pressure is not sufficient to characterize the state of the material.

3 The Origins

3.1 The Middle-Eastern Beginnings

Genuine glass pieces appear in the archeological record in the sixteenth century BCE, i.e. in the Late Bronze age (Chapter 10.2). Regardless of the place(s) where bulk glass was initially made and the sequence of events that led to its production, it is obvious that ancient craftsmen were good observers; otherwise, ceramics, metallurgy, and glassmaking would not have developed as they did over the centuries. Either in a fortuitous way or by trial and error, much experimentation took place to identify the raw materials with which definite goals would be achieved.

Siliceous sand and plant ashes were easily recognizable sources for glassmaking but how *trona* ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2 \text{H}_2\text{O}$), the mineral improperly called *natron* (actually $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$), came to be used and was mined is not known [16]. In glasses, its earliest chemical signatures date back to the beginning of the first millennia BCE [17]. Natron had already long been used for glazes, however, and from Sumerian times it also served a great many purposes in the urban settings of Mesopotamia, as condiment, soap, or product for the embalming of mummies [18], so that a fortuitous reaction with sand in

the way described by Pliny [19] (Chapter 10.0) might have been possible.

The selection of the all-important coloring agents was more tricky because of the differing hues of the raw materials and finished products. The mastery achieved in this respect is nonetheless revealed by the variety of colors yielded by metals such as copper (red and blue-red), iron (black, brown, and green), antimony (yellow), cobalt (blue), or tin (white) ([20], Chapters 10.2 and 10.3). As, for instance, noted by Theophrastus, “A most peculiar earth is that which is mixed with copper, for it not merely melts and mingles with the metal, but also has the remarkable power of enhancing the beauty of its colour” [7]. By observing that small changes in raw materials could result in marked color differences, ancient glassmakers unknowingly discovered how a given property of a material could be varied almost at will in a continuous solid solution. In this way, Mesopotamian glassmakers replicated obsidians, which were thus distinguished depending on whether they were “genuine” or “from the kiln” [20]. In addition, they produced synthetic basalt by firing local silt without apparently recognizing its kinship with the real rock, which was extensively brought from the Zagros and High-Mesopotamia mountains to make steles and statues in Assyria and Babylonia [21].

Because the first glassmakers were by definition entering an uncharted territory, the uses they found for the new material developed along with their understanding of its properties and, especially, of its shapability, which distinguished it clearly from metals and ceramics (Chapter 10.5). It was a well-established Mesopotamian tradition to keep written records of all activities so that the technical nature of some tablets was not particularly remarkable in itself. The fundamental importance of what we term *viscosity* was thus recorded in cuneiform tablets from the fourteenth or twelfth century BCE from Nineveh, found in the library of the Assyrian King Ashurbanipal (r. 668–~628), advising the glassmaker to observe how droplets of glass were sticking to the tip of the rake used to stir the melt.

Mesopotamian glassmakers were thus familiar with stirring (to achieve chemical homogeneity) as well as with grinding and sintering, a process already long familiar to ceramists. They were aware of the deleterious effects of fumes (through vapor-melt interactions) and thus kept recommending “You keep a good and smokeless fire burning.” They used bellows to achieve sufficiently high temperatures and also knew that the color obtained (through redox reactions) depended on whether their pots were covered or not and the door of their kilns open or closed. Glassmakers also mastered quenching procedures by dipping or immersing glass pots in water, and annealed their pieces to prevent them from breaking spontaneously on cooling.

As would still be exemplified by the *venturina* production in seventeenth-century Venice (Chapter 10.7), glass-making operations were nonetheless tricky and not necessarily reproducible. To ensure success through the protection of gods, specific rites were practiced as documented by seventh-century BCE tablets in which procedures for building kilns are reported. The craftsman was, for instance, instructed:

When you set up the foundation of a kiln to [make] glass, you [first] search in a favorable month for a propitious day, and [then only] you set up the foundation of the kiln. As soon as you have completely finished [...] no outsider or stranger should [thereafter] enter [the building], an unclean person must not [even] pass in front of [ritual *Kùbu*-images]. You regularly perform libations offerings before them. On the day when you plan to make the *metal* in the kiln, you make a sheep sacrifice before the *Kùbu*-images, you place juniper incense on the censer and [then only] you make a fire in the hearth of the kiln and place the *metal* in the kiln. [20]

3.2 The Greco-Roman World

The use of the term *metal* to designate glass in Assyrian tablets was not accidental. Not only had glassmakers shared many things with metallurgists in their transformations of earthy materials, but fusibility was another reason for considering glass akin to metals, and not to rocks, which could not be melted at the highest temperatures reached in furnaces. Galen (129–216), the most famous physician of Antiquity, defended himself the analogy between glass, gold, silver, and even iron [22]. As a matter of fact, the Greek and Latin terms *metallon* and *metallum* did not refer to any property of the substances but to a common origin in the ground from where they were extracted [23]: in this respect, sand was for glass the analog of ores for the other metals. In this way glass became part of the grand correspondences established in the Greco-Roman world between the seven mobile celestial bodies (the two luminaries and the five known planets) and the seven metals more or less well identified at that time: the Sun was of course associated with gold, the Moon with silver but sometimes with glass, Mars with iron, Venus with tin or copper, and Saturn, Mercury, and Jupiter with copper, tin, electrum (natural Ag–Au alloys), or with glass [23].

In Egypt, their close association with the imitation of precious stones led the glassmakers to be called *makers of lapis lazuli*. It was also in Egypt that glass began its long and tight association with alchemy (Chapter 10.4, [24]). The dramatic transformations clearly undergone by the raw materials in glassmaking raised the issue of the

kinship between man-made and natural materials and sustained the idea that man could even go farther than nature in his own operations (Chapter 10.4).

Such reflections on glasses considered as molten gems were pursued in Greece where elementary constituents or *qualities* were invoked to account for vitrification (Chapter 10.4). But little was said or claimed about real physical properties. When discussing liquids in *On Generation and Corruption*, Aristotle (384–322) emphasized that their “readily adaptable” shape conferred by their “small particles” made their mutual combinations easy, but mentioned “viscous liquids” only to state that they “produce no effect except to increase the bulk,” without alluding to any glass-forming ability [25]. Likewise, Aristotle did not mention at all glass when he adumbrated the notion of viscoelasticity in his *Meteorology*:

A thing is viscous when, being moist or soft, it is tractile. Bodies owe this property to the interlocking of their parts when they are composed like chains, for then they can be drawn out to a great length and contracted again. [26]

The viscous liquids cited by Aristotle were “pitch and birdlime,” not glass, perhaps because of a more fundamental kinship with metals that was briefly evoked by the statement that “Gold, then, and silver and copper and noted tin and lead and glass and many nameless stone are of water: for they are all melted by heat” [26].

A similar theoretical framework was at the basis of Theophrastus’ reflections in his short treatise *On Stones*. To account for the formation of slags (Chapter 7.4) during smelting operations, Theophrastus thus stated that

When silver and copper and iron become fluid, the stone from them becomes fluid at the same time, possibly owing to the moist character of its constituents or possibly indeed through the agency of the metals.

Theophrastus also paid attention to actual glassmaking. Because the kinship of obsidian and man-made glasses was early recognized, of special interest are his remarks about melting experiments made on the well-known obsidian from Lipari island (Southern Italy): “The Lipara stone, which before burning is black, smooth and dense, is not only rendered porous by combustion, but also assumes the appearance of pumice, so that its colour changes along with its density.” Hence, it was obvious that obsidian could not be used in glassmaking. As we now know, the water always present at a few tenths of wt % in obsidian exsolves as bubbles upon heating when the viscosity becomes lower than about 10^9 Pa.s (i.e. at

temperatures of the order of 800 °C) so that, as described by Theophrastus, one obtains a pumice that either quickly devitrifies or is much too viscous anyway to lend itself to any glass-forming operation.

Regarding the fundamental invention of glass blowing made right before the beginning of the Christian era (Chapters 10.3 and 10.5), it will suffice here to recall that the process required a strict control of viscosity during the alternating periods of working and reheating before the final annealing. As for the production of transparent glass that became extensive at the same period, it was relying on the addition of substances now called antimony oxide (Sb_2O_3) and especially manganese oxide (pyrolusite, MnO), the famous *glassmaker's soap* (Chapter 6.2), which had perhaps been an outcome of the making of black glass in Egypt in the fifth century BCE [27]. Thermal shock was another physical process put to use to cut a piece at the desired place and also for severing it from the blowpipe. The dramatic impact of such advances in glassmaking and the practical advantages of glass over metals could have given some credit to the famous legend of malleable glass, shapable with a hammer, told by the Latin writer Petronius (first century CE) in the *Satyricon*: when the emperor was told that no one else than its inventor knew how it was made, he ordered him to be beheaded “because if this invention were generally known we should treat gold like dirt” [28]. If the story has some truth in it, then it might have had as a starting point a parison falling on the ground while being blown and at once recovered by the blower to finish the work [27]. But the fact that Pliny ([19], cf. Chapter 10.0) himself did not take the story seriously has not prevented it from enjoying great success throughout the ages.

3.3 The Western Medieval Literature

In the West, relatively little is known about glassmaking activities after the fall of the Roman Empire. One rare source is the *Etymologies* written in Visigothic Spain by the bishop saint Isidore of Seville (~560–636). Noting that obsidian “is counted as a type of glass. Sometimes it is green and sometimes black, and it is translucent,” Isidore reported that “the highest esteem is granted to clear glass with its close similarity to crystal,” which “used to be made in Italy.” As he explained further,

Throughout Gaul and Spain the softest white sand would be ground with a mortar and pestle, and then mixed with three parts, by weight or measure, of natron, and after being melted it would be poured into another furnace. This lump would be called *ammonitrum*. When heated again, it would become pure, clear glass. [29]

This statement was almost a word by word copy of Pliny's *Natural History* (XXXVI, LXVI, cf. Chapter 10.0), however, so that its actual significance for Isidore's times is unclear. In the Near East, however, it is known that natron production became insufficient in the seventh to ninth centuries possibly from a combination of too high a demand, unfavorable climatic conditions and political turmoil [17] so that *vegetable soda* derived from plant ashes had to be used instead as a flux.

Dating back to the eighth to tenth centuries, some compilations have transmitted recipes dealing with pigments, inks, varnishes, glues, stones, metals, glasses, etc. The best known are the *Compositiones variae* [30], the *De Coloribus et artibus romanorum* transmitted under the name of the seventh-century Byzantine emperor Heraclius (spelled Eraclius [31]), and especially the *Mappae clavicula* [32] whose content and meaningless Latin title today indicate that it originated in Greek alchemical manuscripts from the fourth century [33]. Probably this ancient literature found its way to the West through Latin translations made in Italy in the late eighth century. What is clear is that copyists then kept modifying these compilations by additions and deletions of their own and that quite a few recipes do not make sense technically. Along with correct descriptions of glass polishing or of the red and green colors obtained with copper, the *Mappae clavicula*, for instance, instructed: “Color thin glass pieces, mix and coat them with dragon's blood, and in this way a reddish color will result.” Such technical compilations would be followed by many others: until the fifteenth century, glass recipes are present in more than 120 of them, generally focusing on softening, coloring, and gem counterfeiting [34].

Some compilations incorporated recipes from an Arabic literature that began to be translated in Latin in the twelfth century. From Egypt to Mesopotamia, the ancient glassmaking tradition had become part of the new Islamic world after the Arabic conquests of the seventh and eighth centuries. In Islam, too, marked changes in glass chemical composition took place in the eighth to ninth centuries probably as a result of natron shortage [35]. This was the time when alchemy became extensively practiced and when Jabir ibn Hayyân (eighth to ninth centuries) became a semi-legendary character to whom an immense alchemical literature would be attributed [36]. Although the term *alkali* is the Arabic *al qaliy* (*calcined ashes*) and original processes were devised, new concepts do not seem to have been formulated about glass and its nature. Jabir himself considered it as part of the seven metals and as the best material for making the vessels within which artificial life could be created ([36], cf. Chapter 10.10). Even the great polymath al-Bīrūnī (973–after 1050), who was active in central Asia, devoted more space to poetry than to technical descriptions in the

short section devoted to glass in his celebrated *Book Most Comprehensive in Knowledge on Precious Stones* [37]. His main statement was that glass “is cast from a well-known stone or from sand to which borax has been added. The substance is heated for several days on fire till it accumulates, clarifies and progressively hardens.” That said, al-Bīrūnī simply added that “different colours are imparted to glass while it is being melted. These colours persist.”

From furnaces to processes, the most reliable ancient review of glassmaking is found in the second book of the twelfth-century treatise *On Divers Arts* of the Benedictine monk Theophilus (Chapter 10.9, [38]). Original views on the constitution and properties of glass are unsurprisingly lacking in this work whose goal was to show how God could be glorified by the practice of the most various crafts. Thanks to its technical descriptions and also to the rich medieval Latin terminology it has transmitted, however, this work has been judged to be “one of the three or four outstanding documents in the written history of mediaeval art-technology,” which distinguished itself from the “random conglomerate” of earlier compilations by the way in which it announced “the rational, ordered, unified composition” of fifteenth-century treatises [39].

Another book of the same period deserves a special mention by the original fundamental insights it threw on glass. These were presented in *On the Elements*, a work perhaps written in France toward 1160 by an elusive author named Marius who relied on his own observations to describe how the four elements combined to make up all things from minerals to Man. In his book, Marius was apparently the first author to point out the kinship of glass not with metals, but with ceramics and rocks, and explained in addition how mud was transforming into what we now call metamorphic and igneous rocks under increasingly strong action of subterranean heat. As Marius asked his readers,

Do you also know that the jar of a potter is a kind of glass? But because it was not cooked long, it is therefore not glass. But if it were cooked for a long time by the fire, it would be turned into clear and glittering glass, like the pot of the goldsmith. Now, therefore, you can observe how stones are created in the body of the earth because of insufficient fire; if the fire were greater, the process would be completed and these stones would be turned into glass. Of this sort are the stones we use for the constructions of houses, and marbles of various colors, and the little white stones which are found on the banks of rivers. [40]

And Marius concluded that “there are many kinds of these because of the varieties of earth of which there

are many kinds — I do not mean earth properly speaking — and because of the variation in the amount of heat they receive [40].” But these ideas received little attention as testified by the single extant manuscript of his book, which had to wait until 1976 to be edited and printed.

While miracles would be soon wrought by transparent glass in the form of spectacles (Chapter 10.10), glass was then about to regain in the colored glazing of churches, an importance it had not had since Late Antiquity (Chapter 10.8). Significant innovations (Chapter 10.8) were the production of red glass through complex microstructural effects in the twelfth century and yellow staining with silver salts in the early fourteenth century, followed by the empirical recognition in Venice that purer raw materials were needed to improve quality (Chapter 10.7). Following the use of quartzite pebbles as a source of silica in place of common sand, the complex treatment of soda plant ash made through successive steps of dissolution in boiling water, decantation, filtration, and drying of the final *sale de cristallo* were clearly indicating that a series of well-defined chemical operations was the key to ensure a consistently high quality.

4 The Early Modern Period (Sixteenth to Eighteenth Centuries)

4.1 An Alchemical Backdrop

Glassmaking progress did not affect the old association of glass with alchemy. On the contrary, argued the metallurgist S. Vanoccio Biringuccio (1480–1539) in his *Pyrotechny* (Chapter 10.9), this art was “born from the speculation of good alchemistic savants, through whose efforts it imitates the metals on the one hand and the transparency and splendour of gems on the other.” And although Nature “has produced crystal and all other kinds of gems that are much more beautiful” than glass, Biringuccio added, “no way has yet” been found for working with these as done with glass [41].

The beauty of glass was not necessarily lasting, however, as alchemists had long noticed the degradation of their glass vessels after long exposure to heat and chemicals. The attack of glass by soda and potash was thus described in some detail in several books; for example, in a text attributed to an enigmatic fifteenth-century monk named Basilius Valentinius, probably the pen name of a salt manufacturer named Johann Thölde (1565–1614) who was familiar with chemical processes. Likewise, potassium silicate was produced as *liquor silicum* through reaction of sand with *cream of tartar* (potassium hydrogen tartrate, $C_4H_5KO_6$) by the chemist Johann Rudolf Glauber (1604–1670) after whom sodium sulfate has been named as Glauber’s salt.

This alchemical backdrop would remain clearly present in the reference glass treatises of the seventeenth century (Chapter 10.9). It is, for example, clearly apparent in the *The Art of Glass Making* of Jean Haudicquer de Blancourt (b. ~1650), where one reads: “glass is a perfect metal, since it does not burn more in fire than gold; & that there is only one fire more powerful than that of the common man who can destroy it” [42]. As a reminder of Petronius’ famous story of malleable glass, Haudicquer also mentioned “the Elixir of the Philosophers which makes it malleable, & which converts crystals into very fine precious stones” [42].

But the most dramatic experiments made at the same period were those of the physician and alchemist Jan Baptist van Helmont (1579–1644) who reported that the sand incorporated in glass was actually not dissolved in it because it could be entirely recovered by an appropriate chemical treatment. As van Helmont explained in his *Dawn of Medicine*,

If one melts a fine powder of glass with a large amount of alkali and exposes it in a humid place, one will presently find that all the glass dissolves into a water. If *chrysulca* [mainly nitric acid] is poured on in a quantity sufficient to saturate the alkali, one will at once find that the sand sinks to the bottom [of the vessel] in the same weight as it was before it was used in making the glass. [43]

In fact, van Helmont precipitated alkali nitrates and silica from the aqueous silicate solution. For him, however, the obvious conclusion was that “by means of art, glass returns into its original ingredients once the bond holding them together is broken: the sand can even be regained in the same number and weight” [43]. In other words, van Helmont thought that this experiment with glass had disproved a fundamental tenet of Aristotelian philosophy, namely, the complete homogeneity of mixtures.

4.2 Descartes: The Foundation of a Glass Science

Certainly René Descartes (1596–1650) was not the first observer to be fascinated by the “transmutation of ashes into glass,” as he summarized glassmaking in 1644 in his *Principles of Philosophy*. In this extremely ambitious treatise, his goal was to describe comprehensively the physical world from a few first mechanical principles [44] in the atmosphere of intense intellectual curiosity sustained by the discovery of whole new worlds with the telescope and the microscope (Chapter 10.10). The famous philosopher was also strongly interested in glass in relation to his own optical research that led him to give a theoretical

demonstration of the law of refraction formulated in the early 1620s in the Netherlands (Chapter 10.10). Reflecting on vitrification, Descartes thus explained in his *Principles* that glass,

when still glowing with heat, is fluid because its particles are easily moved [separately from one another] by that force of fire which previously smoothed and bent them. However, when it begins to be cooled, it can take on any figures whatever. And this is common to all bodies which have been liquefied by fire; for while they are still fluid, their particles effortlessly adapt themselves to any figures whatever, and when such bodies subsequently harden with cold, they retain the figures which they last assumed. [44]

At a time when nothing was known about the microscopic constitution of matter, Descartes described in this way not only what we now refer to as the atomic configurations of a material but also the manner in which these vary with temperature. Descartes went on to explain why glass should be annealed because of differential volume contraction on cooling and buildup of what we call internal stress:

glass “is also more fragile when it is cooled quickly than when it is cooled slowly; for its pores are fairly open while it is glowing with heat [...]. However, when glass cools naturally, these pores become narrower. [...] And if the cooling occurs too rapidly, the glass becomes hard before its pores can thus contract: as a result, those globules subsequently always make an effort to separate its particles from one another.” [44]

Although they were heralding the beginnings of glass science, Descartes’ ideas got completely forgotten until the present time [45]. These groundbreaking conceptions probably suffered from the general criticism laid upon the *Principles of Philosophy*. This treatise was judged by many as a “romance” even before the Newtonians rejected his vortices, which played so prominent a role in his wholly mechanical system.

4.3 The Wondrous Lacrymae Batavicae

Descartes’ *Principles* were nonetheless widely read in the seventeenth century. That Newton imitated Descartes by entitling *Principles* his *magnus opum* is clear evidence of the critical interest in Cartesian physics raised in England. Regarding glass, the physicist Robert Hooke (1635–1703) might already have had in mind the *springiness* of the particles implicitly evoked by Descartes when he turned his

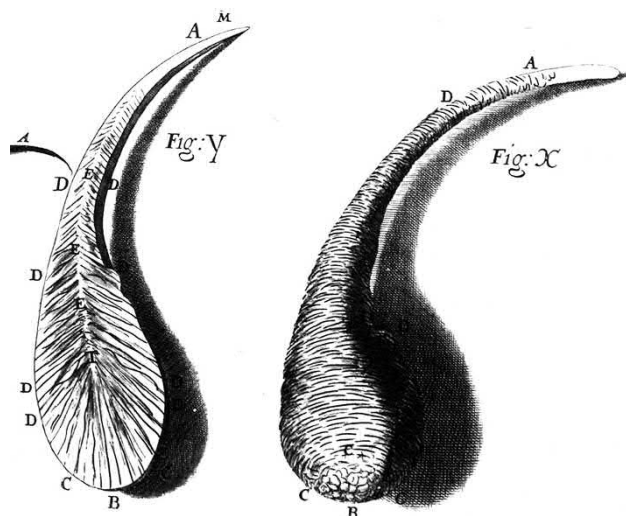


Figure 1 Prince Rupert's drops pictured by Hooke; rupture pattern shown on the left [48].

attention to curious glass drops quenched into water (Figure 1, Section 3.0). This early form of *tempered* glass was probably made before 1625 in Mecklenburg, in Northern Germany, and became called either *lacrymae batavicae* (Batavian tears, in Latin) or *Prince Rupert's drops* long after they had been presented by the German-born Prince Rupert of the Rhine (1619–1682) before the Royal Society of London in 1661 [46].

As originally described [47], these glass beads are remarkably resistant to mechanical shock until a final blow or a breakage of their tail makes them explode and shatter as tiny fragments (Figure 1) even when coated of strong glue or cement. To interpret their instability, Hooke first reckoned that “the parts of the glass” take up more room when hot and fluid than cold and hard, but also that quenching “the glowing metal in the Water makes it of a hard, springing, and rarified texture” so that “the sudden flying asunder of the parts proceeds from their springiness.” In the conclusion of this first study of the mechanical properties of glass, Hooke then stated that “a gradual heating and cooling does anneal or reduce the parts of Glass to a texture that is more loose, and easier to be broken, but not so brittle [48].”

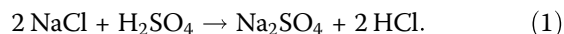
5 The Chemical Revolution

5.1 The New Chemical Researches

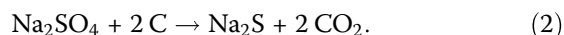
It had in fact long been acknowledged that there was not a single *earth*, but many such as soda, potash (*pot ash*), lime, or magnesia. Although their constitution remained unknown, they could be distinguished by their differing vitrifiability and solubility in water.

The reputedly best soda was produced in Spain from the ashes of a succulent shrub named *barilla* (*Salsola soda*), which is rich in sodium oxalate, tartrate, and other organic salts that decompose upon combustion after which their ashes combine with atmospheric CO₂. Known as *Alicante soda*, it was far from being pure sodium carbonate with the following average composition: carbonic acid (16.7 wt %), charcoal (15.0%), lime (6.4%), magnesia (2.2%), alumina (2.3%), silica (7.3%), free soda (14.6%), sodium sulfate (4.2%), sodium chloride (2.2%), potash (3.1%), water and other volatiles (26.0%) [49]. A simple way to increase its purity was to take advantage of the fact that, in contrast to their *alkaline* counterparts, *alkali earths* were soluble in water. This purification did not have only advantages; however, as was noticed by the future Saint-Gobain director Pierre Delaunay Deslandes (1726–1803) who reckoned in 1756 that lime then needed to be added to the batch to ensure the quality and workability of the glass [50].

Because of the high cost of imported soda and the need to satisfy an increasing demand for products ranging from soap to glass, the French Academy of sciences unsuccessfully offered in 1775 a price for the production of pure soda from salt. Various attempts were then made before the chemist Nicolas Leblanc (1742–1806) patented in 1792 a process for producing synthetic soda from salt, sulfuric acid, coal, and limestone [51]. As understood only toward the end of the nineteenth century, hydrochloric acid and sodium sulfate (*salt cake*) are first produced by the reaction of salt with sulfuric acid:



The salt cake reacts with coal to reduce the sulfate to sulfide



The sulfide then reacts itself with crushed limestone to yield a mix of soda ash and calcium sulfide termed black ash:



In a final leaching step, the black ash dissolves in water and soda ash is recovered by evaporation of the solution. Because of its elevated cost, the Leblanc process did not meet with an overwhelming success in glassmaking. It was in particular cheaper to follow the simpler procedure established by Gehlen in 1810, which consisted in effecting the Leblanc reactions in the batch itself with about 100 parts of sand, 50 of Glauber's salt, 17–20 of powdered quick-lime, and four of charcoal [2, 3]. But an undesired greenish hue was obtained in this way, which was strongly detrimental to the quality of the expensive plate glass. Chemical analyses performed by Pelouze showed that this hue was originating in slight iron contamination caused

by the reaction with the pots of the excess sulfuric acid present in sodium sulfate, which thus had to be of a high purity [49]. Sodium carbonate – the major chemical produced at that time – nonetheless remained produced with Leblanc's method until the early 1860s when the less-expensive Solvay process was invented (Chapter 1.2). The carbonate then slowly supplanted the sulfate as a sodium source as it was ensuring faster sand digestion and thus shorter melting reactions. Because its major advantages for the fining process had been recognized, however, the sulfate was not completely eliminated. It remains today the main agent used for chemical fining (Chapter 1.3).

5.2 The Discovery of the Elements

Compared with earlier glass treatises, those published from the nineteenth century clearly differ by their numerous tables of chemical compositions. The change was abrupt. In the seventeenth century, as noted by W.E.S. Turner (Chapter 9.12), “there was no realization of the complexity and inconstancy of the glassmaking salt, containing as it did the carbonates of sodium and potassium, calcium and magnesium (these last two in large proportions), of chlorides, sulfates, and phosphates, with silica, alumina, and minor constituents” [52]. Although sodium and potassium salts could at last be differentiated in the mid-eighteenth century, the existence of alkali elements would remain debated until the beginning of the following century when they were at last identified at the same time as the alkaline earths.

Knowing of what the traditionally used salts were made was only a first step toward the modern notions of stoichiometry and chemical composition. Four theoretical concepts derived at the turn of the eighteenth and nineteenth centuries were also needed, namely, (i) the law of definite proportions stated in 1794 by Joseph Proust (1754–1826) according to which chemical elements are present in fixed weight ratios in a given compound; (ii) the first atomic theory formulated by John Dalton (1766–1844) in 1803–1806; (iii) Gay-Lussac's law of combining gas volumes (1808); and (iv) the hypothesis advanced in 1811 by Amedeo Avogadro (1776–1856) that equal number of molecules occupy equal gas volumes.

At the end of the eighteenth century, the new chemical system propounded by Antoine-Laurent de Lavoisier (1743–1794) had opened completely new horizons. As Lavoisier stated himself in his famous *Elements of Chemistry*,

It is likely that we know only some of the metallic substances that exist in nature; all those, for example, that have a greater affinity for oxygen than for carbon, are not prone to be reduced or brought to a

metallic state, & they should present themselves to our eyes in the form of oxides, which we mistake for earths. [53]

In a system that associated a *base* with the new element oxygen in all earths, the problem was to decompose the earths to isolate their bases. In this respect, silica was raising a special difficulty because its remarkable purity in the form of crystal rock could suggest that it was actually a base itself and not an oxide. But attempts at isolating a base from alkali and alkaline earths failed until the invention of the electric pile by Alessandro Volta (1745–1827) and its use in *electro-chemical* analyses of matter.

In his first electrolysis experiments on alkali salts, Humphry Davy (1778–1829) realized that their saturated aqueous solutions were inadequate because water decomposition into oxygen and hydrogen was occurring instead. Made either in air with molten soda in platinum spoon or in glass tubes with wet soda, the experiments were difficult because of the instant combustion of the *bases* of potash and soda in air or of their quick reaction with glass. “Like the *alkahests* imagined by the alchemists,” noted Davy, these bases “acted more or less upon almost every body to which they were exposed” [54]. In spite of the difficulties also met to determine their properties, Davy determined that they were in 86.1 : 13.9 and 80 : 20 weight ratios with oxygen in potash and soda, respectively (actual values: 83 : 17 and 75 : 25). Problems to isolate the bases of the alkaline earths were greater still but those of lime, magnesia, and barite and their properties were nonetheless described shortly afterward [55]. Because the bases of silica and a few other earths did not yield, Davy noted [55]:

Had I been so fortunate to have obtained more certain evidences on this subject, and to have procured the metallic substances I was in search of, I should have proposed for them the names of sili-cium [from the latin *silex*, chert], alu-mium, zirco-nium, and glucium [beryllium].

Going one step farther than Gay-Lussac and Thénard with the same procedure, it was eventually Berzelius who isolated the base of silica, which he found to be in a 48.2 : 51.8 (47 : 53) weight ratio with oxygen, and guessed to be in a 1 : 3 atomic ratio [56].

6 The Crystal Connection

6.1 The Early Glass Ceramics

In the early eighteenth century, much work was done to understand how porcelain was made and, thus, how to imitate at a lower cost the expensive Chinese ware

imported. From his own experimental investigation, the naturalist and physicist René-Antoine Ferchault de Réaumur (1683–1757) understood that porcelain owed its properties to a starting mix of clay such that the material was undergoing partial melting at the high temperatures of the furnaces, which made the product intermediate between terracotta and glass [57]. On the other hand, glassmakers knew well that too much time spent at temperatures appropriate for blowing causes partial transformation of the glass to a whitish material that could no longer be blown. Réaumur figured out that by *devitrification*, one could bring the glass partially back to its initial state and, thus, produce a *glass porcelain* of an admittedly lower quality, but at a much reduced cost. After extensive experimentation, Réaumur found that only some glasses yielded the white material he was looking for [58]. The new product would be called Réaumur's glass porcelain (Figure 2).

In Scotland, the glass–crystal relationship was then considered from a completely different standpoint within a debate that was opposing naturalists about whether water or fire was the main geological agent. When the physician James Hutton (1726–1797) explained that the Earth is a heat engine that gives rise to the great cycles of erosion, sedimentation, petrification, and finally mountain-building, his young friend James Hall (1761–1832) thought that experimental support could be given to these ideas. As a volcanic rock, the iron-rich and SiO₂-poor basalts (Chapter 7.2) were assumed to have attained their present positions “in a state of igneous fusion” [59]. When melted in a glass furnace, however, basalt yielded a glass and not the stony rock observed, which seemed to contradict Hutton's theory. Hall thus thought that during its “slow refrigeration in the bowels of the earth,” the molten mass “had undergone a change similar that of glass into Réaumur's porcelain; and that by crystallization it had lost the vitreous, and assumed the stony character” [59]. Experiments made by Hall on different kinds of lavas in fact showed that a glass was each time obtained upon rapid cooling of the melt, whereas annealing or slow cooling resulted instead in crystallization identical in all respects to that of the original lava [59, 60]. The kinetic nature of vitrification had thus been demonstrated.

These conclusions were soon put to practical use. In France, the chemist Jean-Antoine Chaptal (1756–1832) used basalt as a cheap starting product for the industrial production of bottles in Southern France [61]. After some success, his efforts ended in failure because composition variations of the lava caused melting difficulties and devitrification problems, which did not motivate attempts at solving them because market conditions were favoring clear glass bottles. Molten basalt had thus to wait the very high cooling rates achieved in the production of rock

wool to become of real interest in glassmaking (Chapter 9.3).

6.2 From Melting to Crystallization

Another important advance made at that time was the melting of quartz. With a blowpipe burning an oxygen–hydrogen mix, the Genevan-born British physician Alexander Marcet (1870–1923), a close friend of Berzelius, first vitrified silica in 1813 in the form of small needles [62]. In larger quantities, Marc-Antoine Gaudin (1801–1880) then succeeded in 1839 to draw fibers that were “resembling steel in elasticity and tenacity” [63]. After three and a half millennia of glassmaking, the very high temperatures required for melting silica without a flux had been made possible by the discoveries of oxygen and hydrogen and of their combustion mechanism. According to a seventeenth-century account [64], the Berber poet and astrologer 'Abbas Ibn Firnâs (d. 987) made glass from “stone”. Based on an ambiguous meaning of this term, a common interpretation that he vitrified quartz thus is an unfounded claim.

Flow during the long heat treatments required for the production of Réaumur's porcelain made it difficult to keep the complex shape of the original glass piece. Large plates could in contrast be readily produced, which appeared to be much harder and more resistant to thermal shock than the original glass [65]. These advantages of what we now call *glass ceramics* (Chapters 7.11 and 8.5) were thus already recognized at that time. Regardless of high production costs, what probably prevented applications was rapid alteration in air, for instance, shown by the surface formation of potassium carbonate [50].

Although Réaumur's goal had been to *devitrify* partially glass, the nature of the actual transformation effected long remained debated [50]. Was it simply a physical modification of the glass or the precipitation of crystals of a well-defined composition, which thus differed from that of the glass? Important features supporting the latter interpretation were observed by Théophile-Jules Pelouze (1807–1867) in extensive experiments on Réaumur's porcelains. As summarized by Pelouze, “crystalline nuclei” (i) appear at the glass surface; (ii) grow from both sides toward the interior of the plate; (iii) disappear upon heating at temperatures not higher than those at which the starting glass was melted; (iv) reform upon cooling without any weight change; (v) grow with a kinetics that depends much on composition (for example, fast for sodium trisilicate but vanishingly low for a potassium and calcium borosilicate); and (vi) have a growth rate considerably increased by the introduction of refractory material, sand, ashes, or even batch or glass powders [66]. The difference between what is now termed

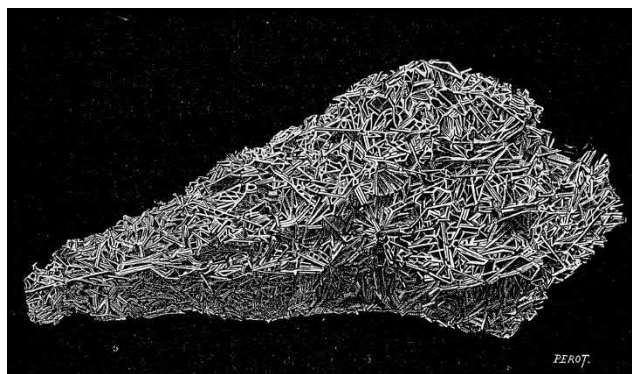


Figure 2 Crystal precipitation in a piece of Réaumur's porcelain. Engraving from [50].

homogeneous and *heterogeneous* nucleation was thus also clearly pointed out.

At the end of the nineteenth century, the kinetics of the process was studied in more detail by Gustav Tammann (1861–1938) who established that homogeneous crystallization depends on heat flow and proceeds in two steps, namely, the initial formation of “crystallization centers” followed by growth of the macroscopic crystals [67]. For both nucleation and growth, the rate varies with temperature according to bell-shaped curves (Figure 3), the growth rate vanishing by definition on the high-temperature side at the melting point of the crystal or liquidus temperature. In quenching experiments performed on 153 liquids of many kinds, vitrification was obtained 59 times, which led to the conclusion that most liquids could vitrify, at least in small amounts, if cooled rapidly enough [68]. That the ability of a liquid to supercool depends on the nucleation and growth rates of crystals was in addition for Tammann the “key to the relation between glasses and fusions. A glass is a non-crystalline, strongly supercooled melt” [69], without any definite melting point upon heating to high temperatures.

7 The Multiple Roots of Glass Science

7.1 Composition Innovations

In the seventeenth-century, the production of *flint glass* in England by addition of large amounts of lead oxide to the composition was a forerunner of future changes made in glass composition to yield new, special properties (Chapter 10.10). Because index of refraction scales with density, crystal glass had a distinctly bright and vivid appearance, which instantly met with popular and optical success. Another new family of glass appeared at about the same time in Bohemia. There, potash-lime glass was made from saccharoid limestone, potash-rich

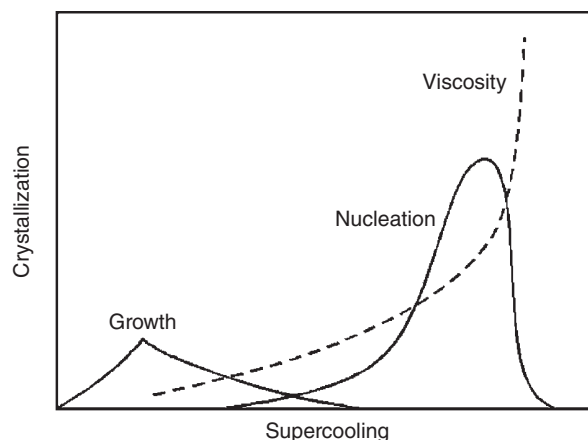


Figure 3 Tammann's depiction of the rates of crystal growth and nucleation with increasing extent of supercooling for a glass-forming liquid whose viscosity increase is also sketched. After [68].

pine-tree ashes, and hyaline quartz as a substitute for rock crystal, which had been extensively mined for the purpose of carving beautiful vessels out of large pieces. The new glass ensured great clarity, even for big pieces, could be ornamented with enamel because it could sustain high temperatures without softening, and for this reason proved to be most valuable for chemical experiments (Chapter 10.10).

Along with flint, Bohemia glass was extensively investigated by the polymath Mikhail Vasilyevich Lomonosov (1711–1765) who wanted to create a glass factory for the production of colored mosaic pieces, beads, pearls, and other fancy or decorative items not made in Russia at that time; before the plant opened in 1753, Lomonosov had already synthesized more than 3000 glasses, which gave him the complete palette of hues he needed to cater to the Imperial court [70]. In practice, this work was restricted to the potash-lime-silica and potash-lead-silica systems to which a host of coloring agents were added [71]. But it suffered from the fact that it was done in the last days of the *phlogiston*-dominated old chemical system and that Lomonosov was perhaps too busy with his numerous scientific endeavors and the management of his glasswork to be interested in glass itself.

In contrast, the discovery of alkali elements and the possibility to analyze them gave a much sounder basis to the study of what came to be called *water glasses* (Chapter 7.5) by the chemist and mineralogist Johann Nepomuk Fuchs (1774–1856) who described new applications such as fire protection for theater curtains [72]. But the compositions of the most common kinds of glasses were not determined at once, as noted in 1830 by Dumas who distinguished soluble, Bohemia, crown, window, plate, bottle, flint, and strass glasses in one of

the first systematic determinations of chemical compositions [73], and got also interested in those of ancient glasses. Since chemical analyses of minerals had clearly shown the existence of stoichiometry relations, Dumas wanted in fact to check the commonly held idea that glasses are “indefinite mixes of various definite silicates”; to his surprise, however, he thought to have found that the very best crown glass was “a definite compound almost as exact as some mineral species.”

Other insights came from investigations of geological materials in which Fuchs participated among many other investigators. Rocks differ widely in the way they react at high temperature. Granite, for instance, is readily melted. From the early nineteenth century, most oxide and sulfide rock-forming minerals were successfully synthesized in the laboratory by mineralogists (e.g. [74]). Efforts were even made at reproducing the texture of rocks. This work involved more than the very few metal oxides that had been used for making glass from the Late Bronze Age. Leaving aside coloring elements, whose concentration is low, these were the oxides of silicon, sodium, calcium, aluminum, potassium, and lead. Boron, in the form of *borax* (actually various hydrates of sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$), and phosphorus from the *microcosmic* salt $[\text{Na}(\text{NH}_4)\text{HPO}_4]$ (Chapter 7.9) were already known at the end of the eighteenth century to be very efficient fluxes, but these rare materials were so costly that their use was restricted to vitrification assays [1].

A few decades later, the vitrifiability issue was re-examined for a variety of elements recently discovered or not. Interest was again paid to phosphorus, from which a glass termed Graham’s salt $[(\text{NaPO}_3)_6]$ had been produced in 1833 (Chapter 7.9). From 1862, the minister William Vernon Harcourt (1789–1871), best known as a founder in 1831 of the British Association for the Advancement of Science, incorporated 14 new elements in 166 different glasses, which he supplied to the physicist George Gabriel Stokes (1819–1903) for optical investigations [75]. Harcourt even discovered the glass-forming ability of B_2O_3 and P_2O_5 , but his efforts had little practical applications before Michael Faraday (1791–1867) realized that addition of boron oxide was a simple means to obtain more homogenous glasses for better optical performance [76].

In Germany, the great optician Ernst Abbe (1840–1905) wondered whether the narrow range of chemical composition of glass was the reason why both refractive index and dispersion (Chapter 6.1) were always increasing in a way similar to density. Was it also the reason why lenses had known little improvement since the invention of flint glass? At Abbe’s instigation, Otto Schott (1851–1935) began in 1881 systematic investigations of the density–optical property relationships of silicate glasses in a work supported by a scientifically oriented

German government. A result was the first commercial production of borosilicate glasses for optical applications. By using all the elements known at that time, Schott could incorporate 28 of them in concentrations higher than 10 wt % [77]. Introduction of barium, a heavy element, for instance, caused an increase of the refractive index of glass without increasing the dispersion. Such observations proved especially useful for microscopy and photography applications. From this work, it became possible to tailor a glass composition for a given specific application as conveniently summarized by the so-called Abbe diagram (Chapter 6.1), in which the range of values that can be obtained has tremendously increased over time (Figure 4).

Further progress in this respect resulted from specific needs. In the United States, a search was, for example, made for glasses with low thermal expansion coefficients because the lights of train cars were breaking under the thermal shock caused by heavy rains. Addition of boron oxide for improving the homogeneity of optical glass already had been described by Faraday [76]. After having also been used by the Schott company to make glass for more stable thermometers, borosilicates resulted in 1908 in the invention of Nonex glass by Corning Glass Works. This lead borosilicate glass was an instant success, but sales soon dropped because the material no longer needed replacement [79]. The use of glass for cooking ware was then considered, but lead-bearing materials were unsuitable for such an application. Further research eventually resulted in 1915 in the famous sodium borosilicate glass dubbed Pyrex, which has extremely small coefficients of thermal expansion ensured by the presence of about 12 wt % B_2O_3 (Chapter 7.6).

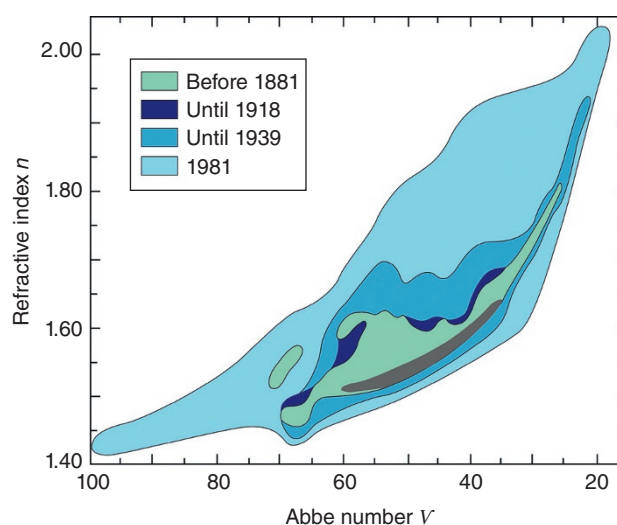


Figure 4 The effects of chemical diversification on the refraction and dispersion of oxide glasses as a function of time (after [78]).

The increasing diversity of chemical composition made possible prediction of a given physical property from the composition of the glass. Near room temperature, linear variations of various properties of silicate glasses were observed as a function of the concentration of oxide components (e.g. [80]). Further experimental work revealed deviations from additivity, which were incorporated in more complex models [81]. However, no such effort could be attempted for melts because experimental data would be badly lacking for a very long time.

7.2 The Contribution of Physical Chemistry

It was a cosmological problem that first awakened an interest in the physical properties of melts [82]. According to ideas formulated by Descartes in his *Principles of Philosophy* and then by Leibniz (1646–1716), the Earth had originally been completely melted. Buffon (1707–1788) found support for this thesis in the fact that granite, which was making most of the Earth's crust, could vitrify readily. Buffon was thus led to think that its age could be determined from the time that had been needed to reach its current surface temperature. After him, Joseph Fourier (1768–1830) derived his celebrated heat equation to give a firm mathematical basis to this exercise but appropriate thermal data were lacking to solve it. It was thus to remedy this situation that William Thomson (1804–1907), better known as Lord Kelvin, inspired in England the first measurements of the enthalpy of melting [83] and in the United States of the variation of the melting temperature of a rock with pressure [84].

Geologists were then beginning to determine also the viscosity of magma either from field observations [85] or from direct measurements on molten minerals and rocks [86]. Viscosities also became systematically measured in glassmaking contexts as exemplified by the basic soda-lime silica compositions [87]. From the early nineteenth century, most oxide and sulfide rock-forming minerals had been successfully synthesized in the laboratory by mineralogists (e.g. [74]). But the notion that minerals and their assemblages had well-defined pressure and temperature stability ranges would be lacking until the new science of chemical thermodynamics was established by Josiah Willard Gibbs (1839–1903) [88]. Following Kelvin's impulse, a group of scientists desired to apply Gibbs' principles to the determination of solid–liquid phase-equilibria in oxide systems relevant to geology. They managed to get the support of the steel tycoon Andrew Carnegie (1835–1919) to create in 1905 the Geophysical Laboratory of the Carnegie Institution of Washington where systematic phase equilibria determinations in two-, three-, and multicomponent systems would be pursued during more than half a century by Norman L.

Bowen (1887–1956), George W. Morey (1888–1965), and many other workers [89].

Of particular importance in this respect was the development of platinum-based thermocouples, calibrated via gas thermometry, which made accurate measurements of high temperatures possible [74]. A significant advance was the thermodynamic temperature scale rapidly established up to 1755 °C at the Geophysical Laboratory to which the e.m.f. of Pt–Rh and Cu–Constantan thermoelements were referred [90]. With the quenching method designed to establish phase equilibria for systems in which transformations tend to be extremely sluggish [91], work was first devoted to the phase diagrams of binary systems with Al_2O_3 – SiO_2 [92, 93], of the CaO – Al_2O_3 – SiO_2 ternary [94] and in addition led to the discovery of liquid immiscibility in binary alkaline earth silicates [95]. Such activity was relevant not only to geology, but also to glassmaking either directly or indirectly through the fundamental benefits drawn for the improvements of refractory materials and of optical glasses [96–98].

Of particular importance to metallurgy was also becoming the physical chemistry of silicate liquids because of the role played by the silica-poor slags in blast furnaces in metal processing and refining (Chapter 7.4). It had been realized in the nineteenth century that desulfurization and dephosphorization of the metal could be controlled through exchange reactions with the slag phase. Thanks to the advances already made, it appeared that important insights on these reactions would be gained through their thermodynamic modeling. This is why metallurgists pioneered measurements of the activities of oxides in melts (e.g. [99]) and phase-equilibria calculations (Chapter 5.3, [100]). Particularly in Germany, they also performed extensive measurements of physical properties such as density and viscosity (cf. studies listed in [101, 102]). Likewise, it was with the support of the metallurgical industry that Bockris and coworkers measured the electrical conductivity [103] and viscosity (e.g. [104]) of silicate melts and arrived at the modern picture of partially ionic liquids made up of groups of various sizes.

7.3 Rupture: From Drops to Fibers

Tempered glass long remained a scientific curiosity. The *springiness* of Prince Rupert's drops was consistently assigned to the forced dilation of their interior parts imposed by the quenched surface layers. But controlled HF etching experiments made by Victor de Luynes (1828–1904) showed in 1873 that the extreme strength of a drop is ensured instead by its compressed surface layers whose convergence at the beginning of the tail causes this spot to be the weakest part of the piece

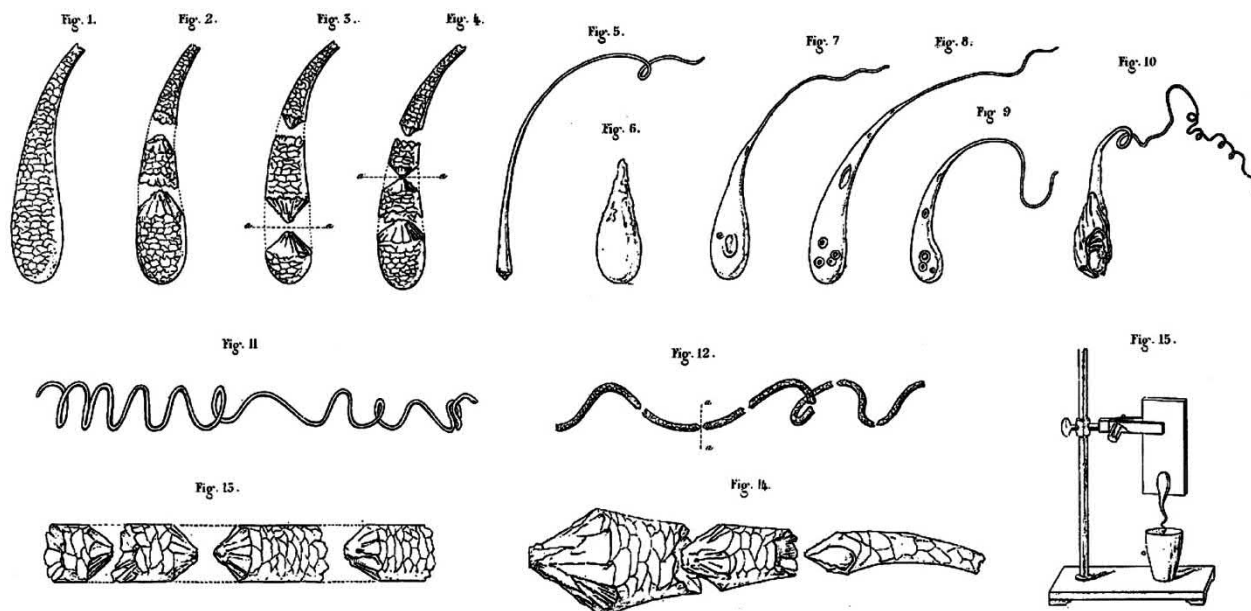


Figure 5 A summary of de Luynes' rupture and HF etching experiments on Prince Rupert drops [104]. Top, left: fracture patterns of drops, the last two sawed horizontally at different places, and drops etched to various degrees without fracture (bubbles becoming apparent). Middle: breakage of quenched fibers. Bottom, rupture of a tempered rod and 1-kg glass piece, and sketch of the HF etching of a drop largely embedded in a plaster plate.

[105]. Upon progressive surface etching, the strength smoothly decreases without any fracturing whereas the lack of any preferred microscopic arrangement within the glass is revealed by the orientation of the conical fracture front toward the particular place of the drop where rupture has been triggered (Figure 5). The unequal "dilation" of the glass layers gives rise to a birefringence also observed under polarized light by de Luynes (cf. Figure III), who concluded that it is the source of the instability that makes the drop explode even under vibrations or temperature changes.

Although tempered glass had long been known, it is unlikely fortuitous that the first process for producing it industrially was patented the following year by François B.A. Royer de la Bastie (1830–1901). His starting point was especially significant because it represented one of the very first applications of glass derived from theoretical considerations. In agreement with de Luynes' ideas, la Bastie thought that the fragility of glass "results from the weakness of the cohesion of its molecules" so that "it may be expected that by forcing the molecules closer together, and rendering the mass more compact, the strength of and solidity of the material should be increased." And since compression is ineffective in this respect, "even when applied to the material in a fluid or soft condition," the solution was to rely on a tempering system "such as is usually applied to steel," which is why la Bastie immersed the hot glass in suitable oil, grease, wax, resin, tar, or pitch [106]. The process

designed in this way for glass sheets did not meet with great success. Reasons were early discussed by the famous engineer Frederick Siemens (see Chapter 10.9), who nonetheless acknowledged that it "caused a great sensation at one time" and induced him to give himself "a great attention to the subject" [107]. Siemens was one of the inventors who patented more efficient tempering procedures, but the technological nature of these advances will not be discussed in this chapter as they are clearly beyond its scope (see Chapter 9.2 instead).

For a material not subjected to extreme stresses, tempered glass may exhibit the most dramatic mode of breakage. In Prince Rupert' drops, the rupture front, for example, moves at velocities measured in the 1450–1900 m/s range [108], such that the ejected glass fragments could break the thick wall of a vessel in which the drop was immersed [109]. But Alan A. Griffith (1893–1963) had not these features in mind when he selected glass to establish his famous theory of rupture, with which the explosive propensity of the drops was at last explained. Griffith was interested instead in the mechanical properties of metals, but he found glass more convenient for demonstrating the considerable lowering of the strength of materials by surface defects [110]. Such practical reasons led him to choose glass fibers for his experiments, which did show a tremendous increase of the breaking stress with decreasing fiber diameter (Figure 6). Because "a fiber consisting of a single line of molecules must possess the theoretical molecular tensile

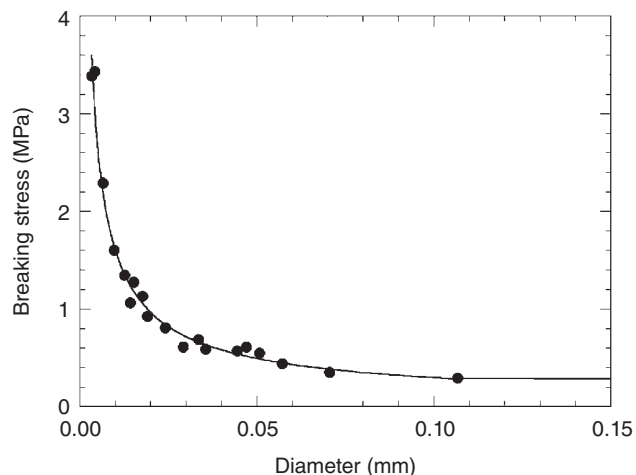


Figure 6 The marked decrease of breaking stress with increasing fiber diameter (1 MPa = 10 bar). Data of [109] for a glass of unspecified composition.

strength,” in the form of fibers glass had more strength than steel, confirming the aforementioned early conclusions of Gaudin on the strength of silica fibers [63]. But two decades would be needed to put this advantage to practical use for materials reinforcement (Chapter 1.6).

7.4 An Elusive Glass Transition

With the exception of the quenching method, which had to be devised for viscous melts, much of the aforementioned physicochemical research was not specific to glass-forming liquids. The new concepts that would be formulated, and lead to a better understanding of glass–liquid relationships, nonetheless relied on the wealth of such data gathered for oxide and organic glass-forming liquids. The lack of heat effect upon vitrification pointed out by Tammann was in particular not real. The outstanding accuracy of the relative enthalpies in crystalline and glassy forms by Walter P. White (1868–1946) made the detection of calorimetric anomalies possible (Figure 7). In what seems to have been the first mention of the glass transition, White related that

several of the glasses show a decided increase in specific heat at some fairly elevated temperature. No explanation has been established for any of these facts. It seems probable that the increase in specific heat would have appeared in other glasses if they had been carried higher. It may be a phenomenon of considerable importance, but for its complete investigation a knowledge of the expansion and perhaps of other properties of the glasses is desirable. [111]

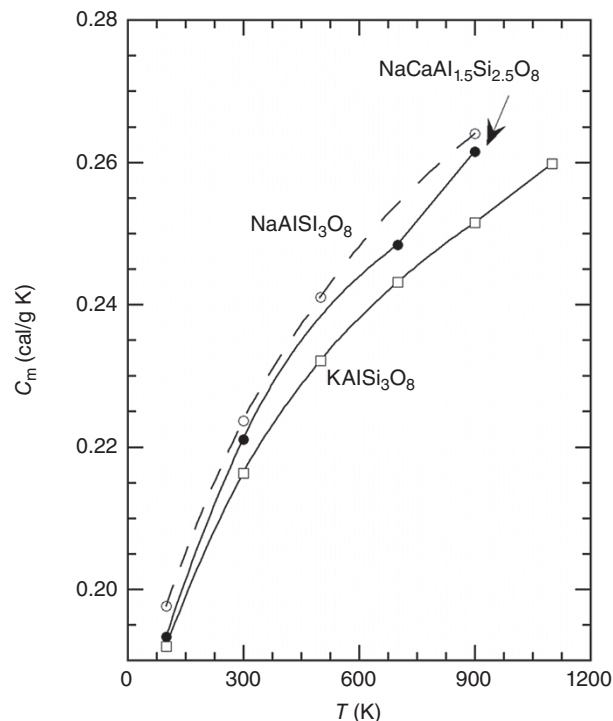


Figure 7 The calorimetric effect of the glass transition: break in the mean heat capacity curve, $C_m = (H_T - H_{273})/(T - 273)$, of $\text{NaCaAl}_{1.5}\text{Si}_{2.5}\text{O}_8$ observed in drop calorimetry experiments. Data from [110].

As a matter of fact, similarly abrupt variations upon heating of a glass had already been observed for the thermal expansion coefficient [112] or the dielectric constant [113], but these anomalies had then elicited little interest. A few decades later interest in these phenomena was, by contrast, awakening, especially in relation with the annealing of high-quality optical glasses.

Near the empirical annealing range, anomalous endothermic effects were observed in narrow temperature intervals for other silicate glasses [114]. For a variety of silicate glasses [115], an important observation then was that marked increases in both thermal expansion and heat were taking place in the same temperature intervals (Figure 8). But the interpretation of these phenomena was not yet clear since it was concluded that:

The cause of these phenomena may be the melting of some of the constituents of the glass, or the melting of the compound as a whole. Whether or not we conclude that glass melts or starts to melt in the critical region depends mostly on our definition of solid and liquid” [115].

In the same year 1920, Arthur Q. Tool (1877–1967) and C.G. Eichlin [116] observed that the endothermic effects recorded between 450 and 600 °C for different types of

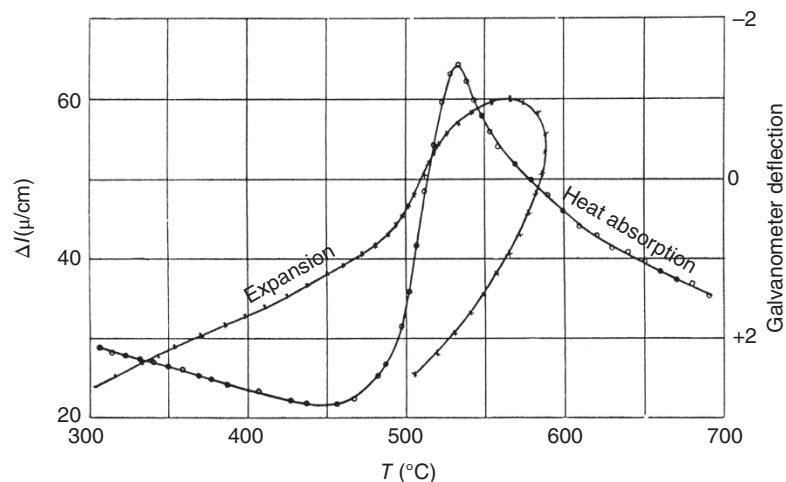


Figure 8 Anomaly of thermal expansion and heat absorption in the same temperature interval upon heating of a light-flint silicate glass. (after [115]).

glasses shift to higher temperatures with faster heating rates and are larger for annealed than for chilled samples (Figure 9). An important conclusion drawn from these results was that annealing “may involve more than the mere removal of stresses” from the glass. But the nature of the other processes involved remained unclear. A possibility was “the formation and dissolution of some

such crystalline structure or other molecular aggregate,” which might also account for the tempering of glass achieved by la Bastie and Siemens without the need of a stress buildup as it was then assumed [116]. Subsequent work by a number of investigators, especially Tool and Eichlin [117], then indicated that a state of equilibrium could be attained through only “molecular rearrangement,” in crystallite-free materials, such that “the density of the glass varies somewhat with the treatment.”

Another approach resulted from the conclusion drawn in 1920 by Gilbert Newton Lewis (1875–1946) and George Ernest Gibson (1884–1959) that, because of the existence of the entropy of mixing,

at the absolute zero there is in general a difference in entropy between a solution and the pure substances of which it is composed. In other words, if we assign zero entropy to the pure substances we cannot take the entropy of the solution as zero [118].

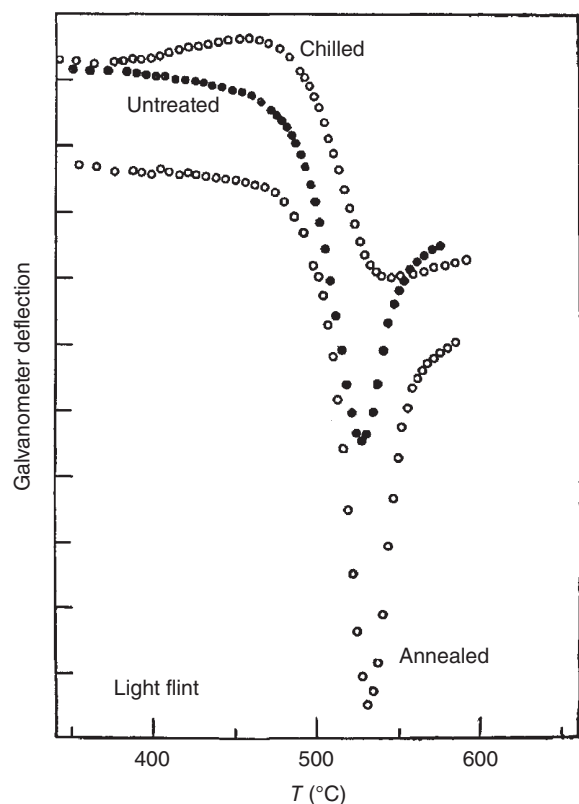


Figure 9 Effect of thermal history on the glass transition of a light flint glass: endothermic peaks recorded in differential thermal analyses. (after [116]).

The existence of a such a residual entropy had a considerable thermodynamic importance with respect to the non-equilibrium nature of glass. It was quickly confirmed by Wietzel who reported that silica glass has at liquid-hydrogen temperatures a higher entropy than crystalline SiO_2 forms [119], but this conclusion was not regarded as definitive in view of the uncertainties affecting the extensive calorimetric measurements needed at high temperatures on which it was relying (Chapter 3.6). Thanks to their low melting temperatures, organic glass-forming systems were lending themselves to firmer statements. From measurements on glycerol $[\text{C}_3\text{H}_5(\text{OH})_3]$, Gibson and William F. Giauque (1895–1982) thus concluded that the excess entropy of 5.6 ± 0.1 cal/mol K found at 70 K for the supercooled liquid over the crystal “will not be appreciably different at the absolute zero” [120].

In these measurements on glycerol, the abrupt 90% heat capacity increase measured for the glass at about 190 K was not commented upon. It was in fact similar to “some remarkable changes” previously observed by Gibson’s team at around 100 °C for ethanol ($\text{C}_2\text{H}_5\text{OH}$) and propanol ($\text{C}_3\text{H}_7\text{OH}$), which had been simply interpreted as “a great increase in the amount of association within the super-cooled liquid” [121].

On the other hand, Alexander A. Lebedev (1893–1969) assumed that glass contained “minute quartz crystals,” forming themselves solid solutions, such that “annealing is not so much the removal of stress as the attaining of complete polymorphic transformation” [122]. His main argument was that the birefringence of optical glass disappears upon annealing near 575 °C, the temperature of the α – β transition of quartz. His views formed the basis for the microcrystalline hypothesis, according to which glass was made up of a disordered arrangement of very small crystals whose structure was similar to that of a stable crystalline form (cf. [123]).

These diverging reflections on the structure of glass were at the roots of the confusion affecting the nature of the physical anomalies observed in glass-forming systems, which apparently White alone had grasped at once as indicating the existence of a new kind of transition. Such divergences notwithstanding, glass formation came to be associated not with any discontinuous change in first-order thermodynamic properties (e.g. volume, enthalpy), but with rapid variations of second-order thermodynamic properties. From their calorimetric measurements on organic substances (Figure 10), George S. Parks (1894–1966) and Huffman eventually recognized the specificity of glass as a distinct state of matter:

While there is no definite temperature, comparable to the melting point of a crystal, at which all properties undergo a sharp change, there is nevertheless a temperature interval, definite and reproducible, in which a number of properties change with a rapidity approaching that observed in the case of the melting process of a crystal. In brief, there is a softening region instead of a melting point. The glass as it exists below the softening region differs so markedly from the liquid existing above that it might well be considered as a different state of the substance. For this reason we have recently suggested the possibility of regarding glass as a fourth state of matter, distinct from both the liquid and crystalline states and yet showing to some extent characteristics of both these states. [124]

Consistent with Descartes’ ideas, a new kind of transition, the glass transition, was at last defined from variations of

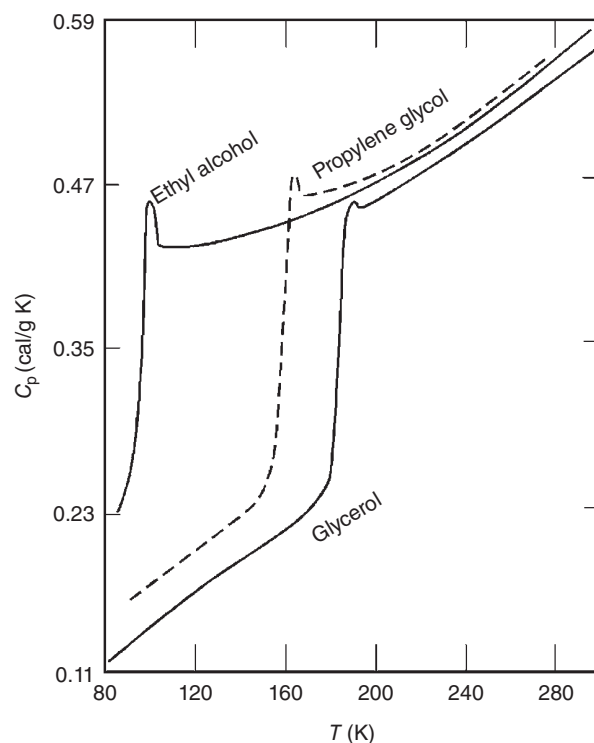


Figure 10 Heat capacity changes of organic substances in the glass transition region (after [124]).

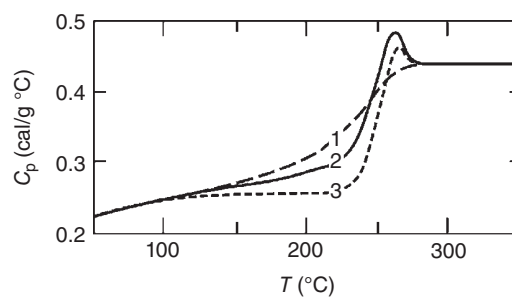


Figure 11 Heat capacity hysteresis observed for the glass transition of B_2O_3 ; measurements made upon cooling (1), heating following rapid cooling (2), and heating following slow cooling (3); data from [125].

second-order thermodynamic properties. Whether in organic or inorganic systems, it was characterized by the same heating/cooling phenomenology as checked by Parks’ team with B_2O_3 [125], which could be accurately performed at relatively low temperatures (Figure 11).

Without any reference to polymorphic-like transformations, the very viscous liquid – which was still in internal thermodynamic equilibrium because its state was determined by only two state variables – was separated from the glass by a transition: occurring over a temperature interval of a few tens of degrees, this transition could

nonetheless be characterized by a temperature denoted T_g . The dependence of glass properties on thermal history first observed in 1845 [14, 15] could then be explained simply in terms of the dependence of T_g on the cooling rate (cf. Chapter 3.6) and the subsequent rate dependence of the loss of internal thermodynamic equilibrium.

7.5 Permanent Compaction

Although temperature is the intensive parameter directly relevant to relevant glassmaking operations, the effects of pressure were also investigated by Tammann. In the same way that one could quench glasses with different thermal histories by changing the cooling rate, one could prepare glasses of B_2O_3 , As_2O_3 , $NaPO_3$, phenolphthalein ($C_2H_{14}O_4$), and other systems exhibiting different permanent compaction by varying the pressure from which they were quickly decompressed [126].

Because the liquid is more compressible than the glass, the observed permanent compaction arises from the fact that only the elastic part of compression is released when the glass is eventually decompressed at room temperature to ambient pressure. The density of a glass thus increases with the pressure at which the liquid is quenched. It offers an indirect way to estimate the compressibility of the liquid [127]. Interestingly, glasses compressed at low temperature to pressures of a few GPa also undergo permanent compaction. This effect was discovered by the pioneer of high-pressure physics Percy W. Bridgman (1882–1961) and Simon for SiO_2 glass compressed beyond 10 GPa at room temperature in minute-long experiments [128]. An 18 % compaction was, for example, observed for a peak pressure of 20 GPa. Especially under nonhydrostatic stresses [129], high pressure could thus induce large irreversible configurational changes at temperatures at which the substance is said to be a glass.

7.6 The Relaxation Problem

Whereas a glass is a hybrid phase characterized by a fixed atomic arrangement, like in a crystal, and by the lack of long-range order, like in a liquid, a melt is a phase whose structure changes rapidly in response to variations of temperature, pressure, and other intensive parameters. Because the term configuration designates any microscopic arrangement of matter consistent with a given macroscopic state of the system, in the 1930s, the physicists Franz Simon (1893–1956) and John D. Bernal (1901–1971) termed *configurational* those contributions to physical properties that are associated with structural changes within the liquid [130, 131]. These manifest themselves most clearly as the abrupt variations of the heat capacity, thermal expansion coefficient, and compressibility at the glass transition.

Configurational properties have also a direct bearing on relaxation, i.e. the variation with time of a given property when the structure of the material adjusts to variations of intensive parameters by tending more or less rapidly toward its new equilibrium configuration. To characterize the rate at which a given property, Y , approaches the new equilibrium value, Y_e , the relaxation time, τ_Y , has been defined as:

$$\tau_Y = - (Y_t - Y_e) / (\partial Y / \partial t), \quad (4)$$

where Y_t is the value actually measured at time t . If τ_Y were constant, i.e. not depending on the instantaneous value of Y , relaxation would be described by a simple exponential law

$$(Y_t - Y_e) = (Y_0 - Y_e) \exp(-t/\tau_Y), \quad (5)$$

where Y_0 is the initial Y value. In other words, after a time τ_Y the variation of Y would represent a fraction $1/e$ of the initial difference from the equilibrium value.

An early landmark of relaxation studies was the analysis of the rate at which the strain and birefringence of a glass-forming liquid varies when the internal stresses built on cooling are progressively released upon annealing [132]. This work was of particular importance for optical glass. A noteworthy practical outcome would be standardization of working operations in terms of viscosity for the strain ($10^{13.5}$ Pa s), annealing (10^{12} Pa s), deformation ($10^{10.3}$ Pa s), and softening ($10^{6.6}$ Pa s) points.

Tool and Eichlin [133] noted that these transformations take place at an “effective” temperature, which was later called *fictive* temperature by Tool [134]:

It is inferred that the physicochemical condition or state of a glass is reasonably well known only when both the actual temperature and that other temperature at which the glass would be in equilibrium, if heated very rapidly to it, are known. This latter temperature has been termed the *equilibrium or fictive temperature* of the glass, and a glass is undercooled or superheated according as the fictive temperature is reached by the actual temperature through heating or cooling, respectively.

For viscosity, Lillie [135] showed how equilibrium properties could be measured via reversal experiments made on samples whose fictive temperatures are initially higher and lower than the temperature of interest (Figure 12). A noteworthy conclusion was that relaxation times depend not only on temperature but also on time and initial extent of departure from the equilibrium state (i.e. fictive temperature). Ever since Tool’s pioneering work [134], this is the reason why relaxation models have become complex (Chapter 3.7) whether individual relaxation times are considered intrinsically nonexponential

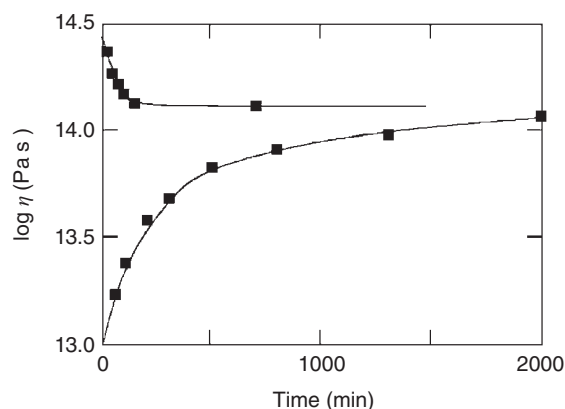


Figure 12 Structural relaxation in viscosity measurements at 486.7 °C on a window glass (after [135]). Lower curve referring to a newly drawn sample with a fictive temperature higher than the run temperature; upper curve to a sample first annealed at 477.8 °C for 64 hours. Thermodynamic equilibrium reached in about 2000 minutes as indicated by the convergence of these curves.

or relaxation is assumed to be made up of many mechanisms with different relaxation times. In this respect, an important question was to know whether the fictive temperature alone is sufficient to characterize fully the state of a glass at a given temperature and pressure, or if more than one such *order parameter* are needed for accurate modeling of relaxation processes (cf. Chapter 3.7). The right answer is the latter: from kinetic experiments made on a borosilicate crown annealed either at constant heating rates or at constant temperature, Ritland showed that the density, refractive index, approach to equilibrium, and thermal expansion did vary for a same fictive temperature [136].

Phenomenologically, the delayed response characterizing a viscoelastic material (Chapter 3.7) was not new when it began to be investigated as a result of the work done in the nineteenth century on various systems in which the mechanical response lasted after the distorting influence had ceased. According to the *superposition principle* then formulated by Ludwig Boltzmann (1844–1906), the actual response of a material subjected to various excitations can be considered as a linear combination of the individual stress–strain relationships [137]. Regarding viscous deformation, homogeneous glass-forming liquids are such that, as stated by Isaac Newton (1643–1727), “the resistance that arises from the lack of lubricity (the friction) is, other things being equal, proportional to the velocity with which the parts of the fluid are separated from one another” [138]. This proportionality between the stress and strain rate of a *Newtonian fluid* was represented by a dashpot in the mechanical model [139] designed by J. Clerk Maxwell (1831–1879), whose other component was a spring

accounting for the elastic response given by Hooke’s law [140]. This model actually works when relaxation is determined by a single relaxation time for processes whose activation energy is constant. Since these features generally do not hold true for glass-forming liquids, another ancient mathematical device that has proven useful in relaxation studies (Chapter 3.7) is the stretched exponential function, $\exp(-t^\beta)$, which had been introduced by Rudolph Kohlrausch (1809–1858) to describe the discharge of a glass-dielectric capacitor [141]. From a dual practical and theoretical standpoint, an important step was recognition in the mid-1920s that the viscosity of glass-forming liquids does not generally follow Arrhenius laws

$$\eta = \eta_0 \exp (\Delta H_\eta / RT), \quad (6)$$

where $A = \log \eta_0$ is a pre-exponential term and ΔH_η the activation enthalpy for viscous flow (Chapter 4.1). To account for the observed nonlinear variations of $\log \eta$ against reciprocal temperature (Chapter 4.1), Vogel [142], Fulcher [143] and Tammann and Hesse [144] proposed instead equations of the form

$$\log \eta = A + B/(T - T_1), \quad (7)$$

where A , B , and T_1 are constants. This so-called VFT Eq. (7) embodies the fact that viscosity would become infinite at T_1 , which is sometimes called the Vogel temperature. Two decades later, Walter Kauzmann (1916–2009) pointed out that the large difference between the heat capacities of the supercooled and crystalline phases of a substance would cause their entropy differences to vanish at temperatures not much lower than the experimentally observed glass transitions [145]. These *catastrophes* yielding negative entropies of melting and the fact that their temperatures are close to the Vogel temperatures have since then been one of the most fundamental features to be accounted for by theories of the glass transition.

7.7 The Beginnings of Structural Studies

There were two basic prerequisites for the determination of glass structures, namely, the actual existence of atoms and the availability of experimental techniques with which their arrangements could be probed. The microcrystals or molecular rearrangements invoked by Lebedev or Tool were thus speculations relying on fragile evidence as X-ray diffraction studies of the main crystalline silicates had just begun (e.g. [146]). Although the first structural studies were done for glasses from the mid-1920s (e.g. [147, 148]), they were inconclusive because adequate methods were lacking to deal with the experimental X-ray scattering curves of amorphous substances (Chapter 1.2).

This interest then raised by glass structure led the young William H. Zachariasen (1906–1979) to reflect in the early 1930s on some fundamental rules that disordered arrangements should follow. His starting point was that a lack of long-range order was not inconsistent with some short-range order imposed by the bonding requirements of each kind of atom. Another important feature noticed by Zachariasen was the small energy and volume differences between glasses and crystals. With the assumption that the new principles of structural chemistry established for crystals should also apply to glasses, Zachariasen postulated that both types of phases share the same basic structural elements. Because they lack symmetry and periodicity, however, glasses differ from crystals by the fact that disorder begins right at the scale of first-neighbor distances. Regarding the extent of medium-range order, Zachariasen thus stood in complete opposition to Lebedev to state in his famous 1932 paper that

An oxide glass may be formed

1. if the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or by oxygen triangles;
2. if these tetrahedra or triangles share only corners with each other;
3. and if some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations. [149]

On the experimental side, the situation changed when the method of Fourier analysis was designed to determine radial distribution functions of liquids [150]. In the 1930s, the method was pioneered by Bertram E. Warren (1902–1991) and his coworkers for oxide and silicate glasses (Figure 13). In studies of SiO_2 and B_2O_3 glass, they confirmed Zachariasen's first rule by showing that Si and B are coordinated by four and three oxygens, respectively, and each oxygen by two Si or B [151, 152]. In addition, they coined the expression *random network* to describe the 3-D disordered arrangement described by Zachariasen. Further work on soda-silica glass [153] showed that two different kinds of oxygens must be distinguished depending on whether they are bonded to only one or to two silicons (Figure 14). Together with these notions of *nonbridging* and *bridging* oxygens, respectively, the distinction between network-former and network-modifier cations was another fundamental concept. Warren and Pincus relied on it to discuss liquid immiscibility in binary metal oxide-silica systems in terms of competition of cations for bonding with nonbridging oxygens, whose outcome is determined by the ratio Z/r_c of the electric charges and ionic radii of the cations [154].

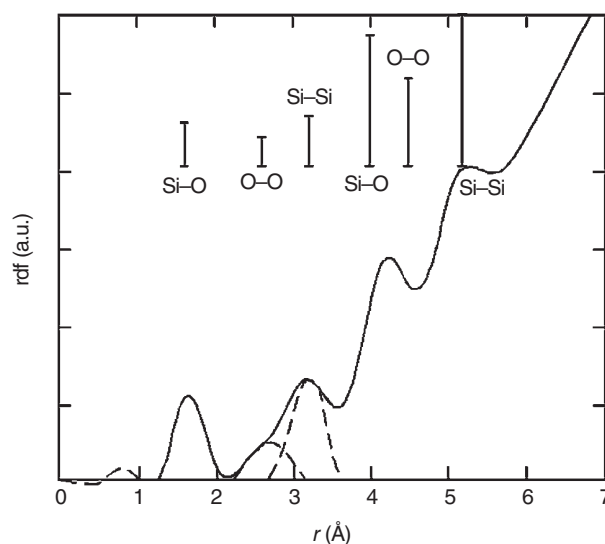


Figure 13 The X-ray radial distribution function of SiO_2 glass (after [151]), the first to be determined for silicate glasses. The peak positions yield the distances between first- and second-nearest neighbors, which can be assigned from known ionic radii or interatomic distances in relevant crystals. For well-resolved peaks, the number of neighboring atoms involved can be derived from the peak areas.

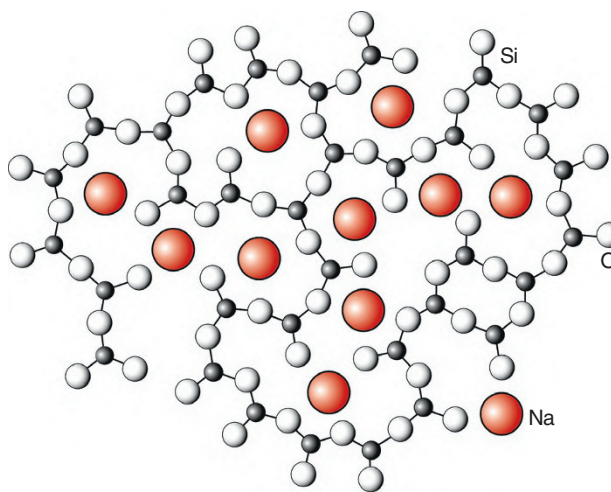
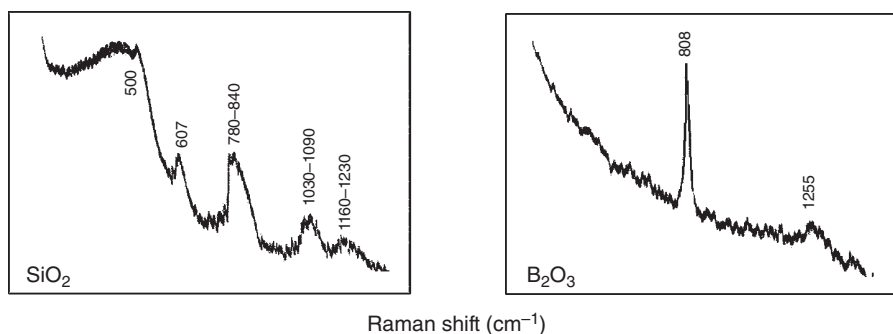


Figure 14 Two-dimensional projection of the structure of a soda-silica glass (after [152]). As derived from X-ray data, this random network also accounted structurally for the existence of gradual (instead of abrupt) softening, viscosity decrease upon Na_2O addition (through fragmentation of the silicate network), and electrical conduction (through hopping of the loosely bound Na atoms).

Even before X-ray diffraction was practiced, other methods were used to investigate glass structure. Right after the discovery of the Raman effect in 1928 [155], the spectrum of quartz was recorded by many investigators (e.g. [156]) and its resemblance with those of silica,

Figure 15 Raman spectra of SiO_2 and B_2O_3 glasses (after [158]). Sharp peak at 808 cm^{-1} in the spectrum of B_2O_3 now assigned to boroxol rings (7.6).



crown, and flint glasses pointed out [157]. Although the Raman signal excited by mercury lamps was weak, the early spectra, for example, recorded for SiO_2 and B_2O_3 glasses compare remarkably well with modern results (Figure 15). For the variety of silicate glasses studied, characteristic features could be assigned to specific structural units present in the structure; although the need for more systematic measurements was pointed out to make reliable specific band assignments, substitution of Al for Si, for instance, indicated a lack of marked structural changes whereas, in agreement with the ideas of Zachariasen and Warren, bands below 550 cm^{-1} were attributed to lattice modes [158, 159].

Instead of the parameter Z/r_c used by Warren and PinCUS [154], Adolf Dietzel (1902–1993) introduced in 1942 the notion of field strength, $I = Z/a^2$, where a is the distance between ions (metal cation and oxygen, in general), to rationalize the systematic variations of devitrification tendency, compound formation, and melting temperatures observed as a function of the nature of cations [160]. That there exists a strong correlation between physical properties and the degree of polymerization of the structure was recognized by Stevels [161, 162] who defined a parameter X to designate the average number of nonbridging oxygens per tetrahedrally coordinated cation; this is of course what is now explicitly denoted by NBO/T (Chapter 2.4). In another approach, the structure–composition relationship was interpreted instead in terms of *structons*, i.e. a limited number of entities made up of a given atom and its nearest neighbors, which changed abruptly with composition [163].

Ironically, the structural heterogeneity claimed by the microcrystalline school bore some analogy with van Helmont's ancient ideas and the strongest evidence for it (see [122]) was in fact the result of metastable liquid–liquid phase separation, which was discovered only in the early 1960s (see [164]). Although random network models are probably too extreme in denying significant medium-range order, the issue of crystalline-like ordering has been raised again recently [165]. Nonetheless, Zachariasen's rules still represent a useful starting point for discussions

of glass structure (Chapter 2.1), which remain themselves common starting points for structural investigations of liquids [166].

8 Perspectives

An interesting contrast is to be noted between chemistry treatises of the eighteenth century and those of the late nineteenth century. Glass was an important topic in the former, in particular because of the basic distinction that was then made between the *vitrifiable* earths and the others (e.g. [5, 167]). In the latter treatises, glass was in contrast paid little attention possibly because the identification of alkali, alkaline earth, and other elements had made the vitrifiability criterion operationally useless in chemistry and perhaps also because glass was no longer thought to raise new important problems by itself. Representative in this respect were the big physical chemistry treatises of Jacobus Henricus van't Hoff (1852–1910) [168], Wilhelm Ostwald (1853–1932) [169], Walther Nernst (1864–1941) [170], or other authorities. In a short section, Nernst, for instance, contented himself to endorse Tammann's ideas about glasses as supercooled liquids by stating that, externally, glass

has the properties of a solid, owing to great viscosity and considerable rigidity, produced by strong mutual action of the molecules. An amorphous body differs from a crystal, however, in its complete isotropy and absence of a melting point; on heating, it passes continuously from the amorphous to the usual liquid state, as its properties show steady change with rise of temperature, and no breaks anywhere. [170]

Ironically, the glass transition was about to be discovered whereas a long chain of studies had already given rise to the glass electrode [171], which would have so much impact on chemistry (Chapter 5.8). It is in fact a recurring theme in history of science that breakthroughs are made

right after important problems seemed to be settled for good.

Building on a long century of advances made in physics and chemistry, a specific glass science crystallized, so to speak, in the critical decade of the 1920s by bringing together physical, chemical, dynamical, and structural features. Of particular importance was then organic substances, which were much more amenable to precise measurements than inorganic glasses. For oxide glasses, this new science was early reviewed in books by Tammann [172] and Morey [173]. Comparison of their contents with that of the *Encyclopedia* illustrates the course followed since then from both experimental and theoretical standpoints.

Like SiO_2 , some “ancient” glasses are now made in completely new ways for completely new applications such as optical fibers (Chapter 6.4) or aerogels (Chapter 8.3). For other applications, wholly original glass compositions have in contrast been designed as illustrated by chalcogenide and fluoride systems (Chapters 6.5 and 6.6). As for organic polymers (Chapters 8.7 and 8.8), they have given rise to major industries because of the ubiquitous uses they have found.

Also noteworthy are the newer fields of metallic (Chapter 7.10) and bioactive (Chapter 8.4) glasses with their serendipitous beginnings and their variety of applications. The former were first produced when Pol Duwez (1907–1984) was attempting to quench metastable crystalline solutions by ultra-fast cooling [174]. They were then engineered as advised by the old glassmaker adage according to which “fusibility is the greatest when the number of bases is the largest” [50], which was previously applied to the so-called “invert” glasses [175]. Although these materials are SiO_2 -poor, they bear a number of other oxides so that they vitrify because their configurational entropy is maximized and both their liquidus and crystal nucleation rates are minimized.

Regarding bioactive glasses, the first one was synthesized by Larry Hench (1938–2015) following a chance conversation in 1967 with a US army colonel who was looking after badly injured Vietnam veterans, and challenged him to produce a material that would not be rejected by the human body [176]. Hench’s first choice was a P_2O_5 -bearing SiO_2 -poor soda-lime silicate composition, which he was expecting to form *in vivo* a hydroxyapatite layer matching well bone tissue. This glass did work well, not as the expected stable material but, rather, as a source of elements for natural regeneration in a way analogous to that of water glass in industrial processes (Chapter 7.5), raising along the way fascinating problems at the frontier between the inorganic and biological worlds.

Of course, it is by definition difficult to guess what additional domains will develop and give rise to new problems

in glass science. In this respect, the fields of ultra-stable and hybrid glasses (Chapter 8.9) have already reached more than a critical size, but there is little doubt that others will keep emerging. From a theoretical standpoint, major challenges remain to be overcome before glass science can be considered fully mature. If one uses structure as a probe of the energetics and dynamics of glass-forming systems, then average structural parameters such as NBO/T are, for example, no real substitutes for the actual distributions of the relevant parameters whose physical significance should be ascertained and variations with temperature and pressure be determined to understand the still elusive nature of configurational changes.

On another basic level, the ever-increasing compositional diversity of glasses makes the yet unsolved problem of the glass transition still more acute as it transcends any features particular to given classes of materials. “The glass transition is not well understood,” already noted in 1972 Angell and Rao [177] who added that “outside the circle of specialists in the area it is not usually even recognized that changes in thermodynamic properties are associated with vitrification.” If the latter statement is now probably no longer valid, the important issue is to know how many more decades will be needed to solve the former problem.

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10.12

Glass Museums

Dedo von Kerssenbrock-Krosigk

Glasmuseum Hentrich, Düsseldorf, Germany

1 Introduction

“A museum is a non-profit, permanent institution in the service of society and its development, open to the public, which acquires, conserves, researches, communicates and exhibits the tangible and intangible heritage of humanity and its environment for the purposes of education, study and enjoyment” [1]. This definition was worked out by the International Council of Museums (ICOM) during its 22nd General Assembly in 2007. It is not fixed, but has evolved “in line with developments in society” and is thus updated by ICOM “in accordance with the realities of the global museum community.” There are few limitations as to what a museum might be, ranging from memorials to places of fun and entertainment. With about 55 000 of them worldwide (and more than 280 in London alone), it seems indeed that we live in an age of museums, where everything one can think of is being collected, conserved, researched, and exhibited.

Such activities can be traced as far back as ancient Mesopotamia: a collection of even then ancient artifacts had been accumulated by Nabonidus (r. 556–539 BCE), the last king of the Neo-Babylonian Empire. It was apparently partly labeled, and stored in a palace that probably served as the residence of his daughter Ennigaldi-Nanna [2]. Whereas it is certainly too far fetched to call this palace a museum (and Ennigaldi the first curator in the history of mankind), as some Internet publications would have it, the idea of assigning value to certain objects and to make them stand out – because of their material, of their role as an idol, as a work of art, as a political statement, or because of other conceivable significances – seems to

be very old. Among the earliest precursors of museums were the treasure houses, of which only the Shōsōin in Nara, Japan, may be mentioned as it has survived for more than 1200 years and still exists: It is mainly composed of the belongings of the emperor Shomu, which his widow Komyo donated to the Todaiji temple in Nara in 756 CE. In 950, further objects were moved to the treasure house. The Shosoin was sealed and kept under the supervision of the Imperial court until the nineteenth century, its contents having been preserved in an outstandingly perfect condition [3].

An important step toward the modern museum was taken when the *Kunst- und Wunderkammer* (Cabinet of art and wonders, in English, or *Cabinet de curiosités*, in French) emerged in the late fifteenth century. It developed in the context of a renewed curiosity in nature and its artificial imitation [4]. These cabinets ideally presented a collection from all spheres of both the natural and the artificial world, and displayed a scientific interest in systematically collecting and studying artifacts. *Kunst- und Wunderkammern* were situated within palaces, and could be spread across a series of rooms, but could also be limited to a single wooden cabinet (*Kunstschränk*). The display of curiosities, treasures, and above all, paintings, became a dominant feature of palaces in the course of the following centuries, and at the beginning of the eighteenth century, palaces began to be enlarged by separate wings dedicated exclusively to the art collections, such as in Salzdahlum (1700) and in Düsseldorf (1712) [5]. At the same time, science museums emerged, such as the Ashmolean that was founded in 1683 as a center for the sciences in Oxford, and only later turned into a museum of art and archeology [6]. In 1759, The British Museum opened its doors to the public as the first national public museum in the world, having been founded six years before with the bequest of the collector Sir Hans Sloane (1660–1753).

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In 1792, the “Musée Français” was established in the Louvre palace. It was a manifest expression of making the private royal treasures the property of the people in the course of the French revolution. The royal palace was turned into a space for the democratic public, and the museum became heir of its former purpose, representing in particular the nation’s glory by demonstrating its past and its conquests, as it were, of art from former great civilizations.

The truly great era of museums started in the nineteenth century, when ancient art in particular was seen as an important model for taste and morale. In the course of industrialization, of World Fairs, and of the competition between nations in encouraging and developing the domestic arts and crafts, museums became a vital instrument of educating the public, and especially the craftsmen and artists [7]. National museums and museums of applied arts were founded in great numbers, such as the Germanisches Nationalmuseum, Nuremberg, and the Victoria and Albert Museum in London, both in 1852, and the Nationalmuseum, Munich in 1855. Their original missions were either to celebrate the nation and its historical products, or – specifically for the museums of applied arts – to encourage the arts by informing and educating craftsmen and artists as well as customers with historical examples and patterns of ornaments and shapes. These missions have shifted substantially over time, but the original concepts continue to shape our general understanding of these institutions as places of collecting, preserving, researching, and communicating our heritage.

2 The Invention of the Glass Museum

When glass started to be produced in the ancient Middle East, in about 1500 BCE, it seems to have immediately been considered a precious material that was worth to be kept as a treasure (Chapter 10.2). Early glass survived in perfect conditions in the tombs of the Pharaohs of the New Kingdom, from the sixteenth to eleventh centuries BCE, which were furnished with glass vessels, inlays, and sculpture of exceptional quality. The Shōsōin, the abovementioned treasure house in Nara, Japan, houses to this day a number of glass vessels dating from the fourth to sixth centuries CE that must have traveled on the Silk Road from the Middle East to Japan [8]. Rarity and distant origin of production may also have been at the core of introducing Byzantine and Near Eastern glass objects into Western medieval church treasures. Glass occupies a place of pride in the treasury of San Marco, Venice [9].

In 1713–1714, King Frederik IV of Denmark had a room in his castle Rosenborg in Copenhagen turned from

a gallery of small paintings into a glass cabinet. To this day, the room houses a glass collection that Frederick had been given by the city of Venice during his visit in 1709 [10]. The collection is of utmost value as a time capsule, a window into a very specific and interesting period of glass production. Venice, or more precisely, Murano, was the world capital of glassmaking at the time (Chapter 10.7), but the pressure from competition with Central Europe and England was mounting. Moreover, the Rosenborg glass cabinet is perhaps the first instance of an entire room being dedicated exclusively to glass. It was displayed following the example of porcelain cabinets that emerged in the Netherlands and became fashionable in Central Europe (beginning with Oranienburg castle in Brandenburg) in the 1660s.

Apart from Rosenborg castle, there have been other prominent displays of glass at the time, such as the Green Vault, established in 1723–1730 in the city palace of Augustus the Strong in Dresden, Saxony, which features an impressive number of gold ruby glass vessels. Yet, such a focus on glass as in the Rosenborg cabinet is not known to have existed anywhere else until the nineteenth century. Both the Rosenborg cabinet and the Green Vault originally formed part of treasuries, and thus were not open to the general public (today, both are very popular museum attractions). And yet, it may be fairly acceptable to call the Rosenborg glass cabinet the first glass museum of the world.

Treasuries have been among the predecessors of some of today’s glass collections. But the emergence of public glass displays within arts and crafts collections, as well as archeological museums, is even more significant. Most of the best public glass collections today have not been turned into autonomous glass museums, but continue to be a part of larger museum entities, such as The British Museum and the V&A in London, The Metropolitan Museum of Art in New York, the Museum of Applied Arts in Prague, the Römisch-Germanisches Museum in Cologne, and so forth. Even the Glasmuseum Hentrich, which bears the title “museum” in its name, is in fact a department of the Kunstpalast in Düsseldorf. If this chapter were limited to glass museums in the strictest sense, all of these collections and many more would have to be excluded. Instead, if only for the purpose of this overview, a “glass museum” shall be defined as any public glass collection whether as a glass museum on its own, or embedded in a larger museum entity; in short, this essay will consider both glass museums and glass collections in museums. “Glass museum,” “glass collection,” and “museal glass collection” will be used more or less synonymously, for the mere purpose of avoiding too much redundancy.

Before delving into the details of glass collections, it should be noted that some museums (or public galleries)

do host noteworthy glass exhibitions without building up a permanent collection of their own. Among the examples are the National Glass Centre in Sunderland (Tyne and Wear, England), as well as the Reiss-Engelhorn Museums in Mannheim (Germany), which cooperate with the Design Museum (mudac) in Lausanne (Switzerland) [11, 12].

3 Glass Museums

It is not within the scope of this chapter to provide a list of all existing glass museums. Each of the nine numbers of the *Bulletin des Journées Internationales du Verre*, published between 1962 and 1983, provides information on the glass collections of one specific country [13]. An *International Repertory of Glass Museums and Glass Collections* has been published in 1966 [14]. The initiative for this repertory came from the Comité international pour les Musées et collections du Verre (today: ICOM Glass), a chapter, established in 1959, of the ICOM. A list of glass collections on the website of ICOM Glass is currently being put together [15]. Such a list is already online for glass collections in Germany, hosted by the website of the Deutsche Glastechnische Gesellschaft [16], and a number of Italian glass museums have been listed on the website of the Italian committee of the AIHV [17]. A list of glass museums in the United States has been compiled and updated since 2008 at the Rakow Research Library of The Corning Museum of Glass and is available there upon request [18]. A brief overview of French glass in museums in France and abroad has been given by Daniel Alcouffe [19, 20]. Similar accounts exist for English [21] and Scottish [22] glass, respectively, as well as for glass museums in the Czech Republic and in Slovakia [23]. There is also, albeit in Japanese, a directory of glass museums, shops, galleries, and studios in Japan [24]. Last but not least, the publications of Helena Horn [25] and Shaun Kiddell [26] should be mentioned in this context.

Depending on their respective roots, their environment, and their mission, glass museums take on quite a variety of roles and characters. The following attempt at a classification may merely serve to understand better just how varied the field of glass collections actually is.

4 Types of Glass Collections

4.1 Princely Collections

No palace of the higher aristocracy in Europe can be imagined without glass – windows, chandeliers, and mirrors were significant features of any of them, and those of pristine quality were more challenging to make than drinking

vessels. Versailles and its *Galerie des Glaces* need to be mentioned here, as well as the palaces of the Stiftung preußische Schlösser und Gärten Berlin-Brandenburg. With its interior mostly unchanged since 1770, Eggenberg castle near Graz, Austria, offers the unique opportunity of experiencing on special occasions the original baroque candle light from glass chandeliers and candelabra [27].

In some cases, a particular king or prince took a particular interest in glass, which resulted in collections such as in Castle Rosenberg and the Dresden Green Vault – already mentioned – or in the Veste Coburg. The glass collection of duke Alfred of Sachse-Coburg-Gotha (1844–1900) has been documented particularly well. There seems to have been a special affinity for glass among members of that family, as the collections of the Palacio da Pena and the Museu de Arte Antiga in Lisbon demonstrate. These ties, and the interest and practice in nineteenth-century glass collecting in principle, are currently being researched extensively [28].

4.2 Museums of Decorative Arts Versus Museums of Cultural History

The Museum of Manufacture, then South Kensington Museum, and today Victoria and Albert Museum was founded in 1852. It followed in principle the structure of the London World Fair of 1851 in that it arranged its collection according to the respective industries ([7], pp. 36–38 and 99–100). This system proved to be a lasting concept that has been followed by many other museums, such as the Austrian Museum for Art and Industry in Vienna (today “MAK”). From the onset, glass formed a class of its own in these museums. It was separated from stained glass, though, thus reflecting the difference in the production of glass vessels from the making of leaded windows. That separation can be felt in glass collections to this day, which – apart from the very few specialized stained glass museums – tend to focus almost entirely on glass vessels and sculpture. The V&A has largely maintained its original concept in that glass is exhibited in a space of its own, if regrettably too small a space to do justice to the size and superb quality of its collection. Some of the best objects are shown alongside other materials in thematically arranged galleries of the museum.

Thematical galleries – period rooms, or other displays of art of one time period – are also an inheritance of nineteenth-century museum concepts, and aimed at the education of a general public in their cultural history. A good example is the Bayerisches Nationalmuseum (Bavarian National Museum) in Munich. It was founded in 1855, and its mission was quite simply to keep the arts and crafts of the past from sinking into oblivion. The collections, consisting mainly of the possessions of the House of Wittelsbach, were organized by Jakob-Heinrich von

Hefner-Alteneck (1811–1903), their director from 1868 to 1886. Hefner realized that galleries arranged according to aspects of cultural history (essentially, period rooms) could display but a tiny fraction of the large collections. He therefore installed “special collections,” which he organized, following the model of museums of applied arts, according to the respective industries [7, p. 126].

Today, just looking at the permanent displays, it may be hard for a visitor to discern whether the respective museum has its roots in an educational facility for the applied arts, or if it originated as an institution of cultural history. The lines have been blurred from the onset. Especially since the 1870s, decorative arts collections were included into museums of art, history, and culture, and vice versa, museums of applied arts began to look for new concepts of display. The Deutsches Gewerbe-Museum in Berlin (today the Kunstgewerbemuseum, Staatliche Museen zu Berlin Preußischer Kulturbesitz), which opened in 1868, had a section on vessels sorted first according to their epochs (Ancient, Middle Ages and Renaissance, Modern) and only then by material. The Metropolitan Museum of Art in New York was founded in 1870 “for the purpose ... of encouraging and developing the study of the fine arts, and the application of arts to manufacture and practical life, of advancing the general knowledge of kindred subjects, and, to that end, of furnishing popular instruction” [29]. In its setup, the museum separates the decorative arts from paintings and sculpture and arranges them according to their periods of style – some spectacular, original period rooms included.

The history and original purpose of a museum not only have an impact on the display of its collections but also guide the specific goals of collecting specimen of various materials. Shapes and ornaments that could serve as models for artists and craftsmen were the focus of the museums of applied arts; objects that typify a certain period and show, beyond their artistic quality, some interesting cultural or historical aspects were sought after by museums of cultural history. If installing a period room, a museum keeper might look out for mirrors and lighting fixtures in particular. Both are remarkably absent, certainly in terms of permanent display, from those collections that tended to separate their holdings by material.

That the intricacies of a collection are shaped by changing interests over the course of time can be demonstrated by the Glasmuseum Hentrich in Düsseldorf, Germany [30, 31] (Figure 1). Its roots go back to the Düsseldorf museum of decorative arts that was opened in 1883. It was geared toward the local and regional craft workshops and industries by providing examples of good artistic craftsmanship (“Vorbilder” and “Muster”), both in the form of real objects and of a library of photographic images. For various reasons, the privately funded



Figure 1 Kunstpalast, Glasmuseum Hentrich. Details of its bright-red “treasure house” of 2006, providing a chronological path through the history of glass on three levels. Source: Photo: LVR-Zentrum für Medien und Bildung, Stefan Arendt.

museum had to close in 1927, and the lions share of its collection was transferred to the newly opened, local Art Museum. The prominent and somewhat disrespectful display of the accession numbers on the objects is characteristic for their use as models. The shape of an enameled beaker (Figure 2) might, for instance, have appealed to a producer of beer glasses, while the decoration could have served as a formidable example of German Renaissance blazonry. This particular glass has not been kept for being outstanding. It is an ordinary, typical, and perfectly sound example of its kind, and the visible number allowed for quick identification and reference.

In the new context of the “Kunstmuseum,” the utilitarian aspect of demonstrating objects such as these to craftsmen completely vanished. Initially, the Kunstmuseum had no use for these collections at all, as it had been conceived as a museum of fine arts. For the next five years, the decorative arts may well have been stored away



Figure 2 Large beaker (“Humpen”), dated 1603, with coats of arms, and prominent display of its museum inventory number. Bavarian Forest, late nineteenth century (before 1887). Kunstpalast, Glasmuseum Hentrich (11275). Source: Photo: LVR-Zentrum für Medien und Bildung, Stefan Arendt.

completely, but they received renewed attention after 1933, at the beginning of the National-Socialist era. While the collection of modern art was to suffer heavy losses because of the Nazi’s aversion against modernism, interest in the decorative arts was growing, and the “importance of the objects” recognized “as expressions of cultural life” [32]. Between 1935 and 1948, three significant glass collections (Lückger of Roman and Medieval glass; Jantzen of European glass, mainly German Baroque and Biedermeier) were purchased, while a fourth attempt at a purchase (collection Eigel) failed. Not only glass was being acquired, but also ceramics, perhaps because both materials were comparatively affordable and allowed to focus on the regional, German art production, e.g. Roman glass from Cologne, Renaissance-forest and enameled glass, and engraved goblets of the Baroque period. The growth of the glass collection may also have been a reflection of Düsseldorf’s international reputation as a center

for glass technology. Until 2005 it was home to the largest glass bottle factory in the world, Gerresheimer Glas, as well as to the German trade association for packaging glass (Fachverband Behälterglasindustrie e.V.), and it continues to host Glasstec, the largest glass industrial fair in the world.

The wave of glass acquisitions in Düsseldorf almost coincided with the respective augmentation of the V&A’s collections: English glass from Mr. and Mrs. C. Rees-Price in 1925, followed by the collection of Francis Buckley, and, in 1936, the donation of Wilfred Buckley’s collection of European glass. Other than the V&A, however, which aimed for an even growth in all of its departments, in Düsseldorf there was a clear focus on glass and ceramics. Today’s quality of the Glasmuseum Hentrich is mainly due to the donations given by the architect Helmut Hentrich in annual installments from 1961 until his death in 2001. Already in the 1970s, his gifts outnumbered the rest of the collection so that in 1995 the glass department adopted his name. From a small number of glass objects within a museum of decorative arts to a collection of glass as an expression of German culture, and more recently to a collection of international glass art, the Düsseldorf glass collection has undergone significant changes, which are all reflected in its present appearance.

Turning a miscellaneous museum collection that includes some glass into a more or less autonomous glass museum seems to be a phenomenon of the twentieth century based on private initiative. This has not only been the case at the Glasmuseum Hentrich, but also at two other institutions that can rightfully be counted among the largest and most varied glass museums in Europe: the Museum of Decorative Arts in Prague and the Grand Curtius in Liège.

The history of glass in Bohemia goes back to the Middle Ages, and the glass industry and trade became a major commercial factor for the region since the early eighteenth century. It therefore does not come as a surprise that glass is the main focus of the Museum of Decorative Arts (Uměleckoprůmyslové museum, or UPM) in Prague. The museum had been founded in 1885 by the Prague Chamber of Trade and Commerce, and received in 1906 the famous glass collection of Adalbert von Lanna (d. 1909) as a donation, followed in 1932 by the bequest of the glass collection of the museum director and scholar Gustav E. Pazaurek (d. 1935). These donations allowed the museum to become the Czech national glass collection, as it were, assisted by the various regional glass collections in Jablonec (specialized on glass jewelry), Nový Bor and Kamenický Šenov (glass heritage of Northern Bohemia), Sazava and Karlovy Vary (see Section 4.5), Klatovy (glass in Southern Bohemia, especially Loetz), as well as in Brno, Liberec, Pardubice, and Železný Brod (M. Hlaves, private communication).

The glass department at the Grand Curtius in Liège, Belgium, plays a special role among glass museums in that it has been the cradle of the two main international research societies in the field of the history of glass. Joseph Philippe (b. 1919), then director of the Curtius museum, had founded the “Journées Internationales du Verre” in 1956 and hosted the first gathering during an ICOM congress two years later. From this initiative, ICOM Glass was formed in 1959 (mentioned above), and the body founded by J. Philippe was renamed in 1967 *Association Internationale pour l'Histoire du Verre* (AIHV, *International Association for the History of Glass* [33]. The foundation for the Liège glass collection was established by the collector Alfred Baar (d. 1907) and his son Armand (d. 1942). Their collection amounted to more than 2400 items, which were given as a loan to the Musée Curtius in 1946, and were purchased in 1952. For many decades since 1959, the glass collection acted as an independent “musée du verre,” but it was reintegrated into the completely refurbished Grand Curtius in 2009. The glass collection has its particular strengths in the field of glass *à la façon de Venise* (Chapter 10.7) which played a significant role in the seventeenth-century Southern Netherlands, and of products of Val Saint-Lambert, at times one of the world's largest glass factories.

A number of museums of decorative arts need to be mentioned here. In the 1970/80s, the directors of the Kunstgewerbemuseum in Berlin, the Museum für Angewandte Kunst in Cologne, and the Museum für Kunst und Gewerbe in Hamburg – Franz Adrian Dreier, Brigitte Klesse, and Axel von Saldern – were all specialists in the history of glass, and thus contributed to the growth, character, and research of their respective collections. The museums of decorative arts in Bremen, Frankfurt, and Kassel host significant glass collections. The Musée des Arts Décoratifs in Paris comprises the most important general collection of glass in France.

4.3 Archeological Collections

Almost all of the abovementioned museums include archeological collections, i.e. excavated artifacts mostly from Antiquity and the Middle Ages (today, archeology can extend into the twentieth century). A clear distinction should be made, however, between museums that acquired archeological artifacts from private collections or in the art market, and those museums that act as the repository for official excavations. With rare exceptions, the possessions of the first group lack proper documentation: it can often not be excluded that they surfaced by illegal diggings, and the original location and context of the finds is either completely lost, or passed on with little reliability.

Very few “official” archeological museums would consider calling themselves a glass museum. One exception is the Museum of Ancient Glass (Muzej antičkog stakla, or mas) that opened in Zadar, Croatia, in 2009. It is dedicated exclusively to archeological glass finds, mainly from the Zadar Roman necropolis and other regional excavations [34]. Archeological collections tend to be of highest importance for our knowledge about the history of glass. Artifacts in these collections usually have a firm date and origin (at least in terms of their use), and can often be tied into a social or cultural context. Related finds may show whether an object has been a rare treasure or a common item of daily life; and comparisons with other archeological collections give clues as to how far certain objects have traveled. Institutions that are responsible for the archeological heritage of a region (not always museums, but also regional offices of ground monument conservation) are not selective, but keep, in principle, every artifact that falls into their realm.

The majority of these finds are rarely exhibited, and glass tends to form but a minor part of the various holdings. Nevertheless, almost every archeological museum owns some glass (provided, of course, that this material had been known to the region that the museum is representing). Significant artifacts of Roman glass (Chapter 10.3), to give an example, can be expected to exist in practically every archeological museum in Italy, and beyond in the former territories of the Roman Empire. The Museo nazionale Archeologico in Naples stands out for its collections of glass from Pompeii and Herculaneum. Roman glass of superb quality is also shown at the Römisch-Germanisches Museum in Cologne or the Römisch-Germanisches Zentralmuseum in Mainz. The Pokrajinski Museum in Celje (Slovenia), founded in 1882, is dedicated to the excavations of the Roman necropolis of Celeia. Only two examples for post-Roman archeological glass collections may be given: among the most prominent collections of the Regional Museum of the city of Biograd na Moru (Croatia) are the finds, glass in particular, from the sixteenth-century Venetian shipwreck that sunk in the Adria near Gnalić. Excavated glass vessels from the Roman period into the eighteenth century are part of the collection and on view at the Museum of London, which is an amalgam of the former Guildhall Museum, an archeological collection founded in 1826, and The London Museum of 1912.

4.4 Scientific and Technical Collections

Scientific collections were among the first to include glass. The Museo Galileo in Florence, Italy, is particularly noteworthy, as it houses a truly special collection that goes back to the seventeenth-century Accademia del Cimento. The collection was rediscovered in 1839 by

the director of the Museum of Physics and Natural History, one of the predecessors of the Museo Galileo, and comprises scientific glass instruments that were produced in Florence since the second half of the sixteenth century [35].

Probably encouraged by the success of the world fairs since 1851, technical museums saw their heyday in the first half of the twentieth century: Before the destructions of World War II, almost 100 museums in Berlin were devoted to the history of technology. It took until 1982 to consolidate the remnants of these collections in the newly founded Deutsches Technikmuseum [36]. Here, glass only plays a minor role, and is better represented in the Museumsdorf Baruther Glashütte in the tiny village of Baruth, south of Berlin: an open air museum and industrial monument tells the story of glassmaking in this valley since 1716, it includes live glassmaking shows, and a permanent exhibition on Reinhold Burger, the inventor of the thermos flask [37]. Further to the West, the Gernheim Glassworks form part of the LWL Industrial Museums and are housed in an original glass cone of 1825. Production ceased in 1893, and the premises were turned into a museum in 1979 [38]. Together, Baruth, Gernheim, and the Glass factory Lamberts in Waldsassen applied for adding the manual production of mouth-blown hollow and flat glass to the German inventory of the intangible cultural heritage of UNESCO, and succeeded in 2015. The Continium discovery center in Kerkrade, The Netherlands, is a hands-on science museum that includes several historical collections. One of these is dedicated to glass, namely to the production of the Kristalunie glass factory in Maastricht [39]. Continium has been founded in 2009, based on a previous institution, the Industrien, which existed from 1994 to 2009.

A more prominent role is given to glass at the Deutsches Museum in Munich, which addresses the whole history of science and technology in Germany. It was founded in 1903 and has featured glass exhibitions since 1906. A room dedicated to glass technology in 1928 was destroyed during World War II. It was augmented into a department of glass technology that existed from 1959 to 1978, and was reinstalled in 1990 (Figure 3). The museum is working on a six-volume series on glass technology, of which four have been published so far [40, 41].

Some companies specialized in glass technology have founded museums of their own. A collection of optical instruments that was established by scientists of the Carl Zeiss company in Jena in about 1900 was turned into the Optisches Museum in Jena in 1922 [42]. The same city houses another glass technological museum, the Schott GlasMuseum und Schott Villa [43]. In Corning, New York, the Corning Glass Works (today Corning Inc.) established the Corning Glass Center in 1951, which



Figure 3 Deutsches Museum, Munich, entrance to department of glass technology, 2012. The white interior creates a demure and scientific atmosphere. Source: Photo: Deutsches Museum.

featured a Hall of Science displaying the proudest achievements of the company, as well as a more general museum of glass [44]. Today, the Glass Center has been completely incorporated into the steadily growing Corning Museum of Glass; the Hall of Science continues to exist within the museum as the Glass Innovation Center [45].

Probably the largest museum of glass technology is located in La Granja, Spain. The Technology Museum of Glass was founded in 1989 and is housed in the spectacularly well-preserved eighteenth-century factory buildings of the Royal Glass Factory of La Granja (Figures 4 and 5). It is dedicated to the methods of glass production of the eighteenth century, and includes both blown glass and stained window glass, the latter being represented by the workshop of the brothers Maumejean, a French–Spanish company of the late nineteenth and early twentieth centuries. The museum also includes collections of bottles from various European factories, as well as crystal from the La Granja production and contemporary glass art. It is accompanied by a glass school and a large studio glass workshop ([46] and P. Pastor Rey de Viñas, private communication).

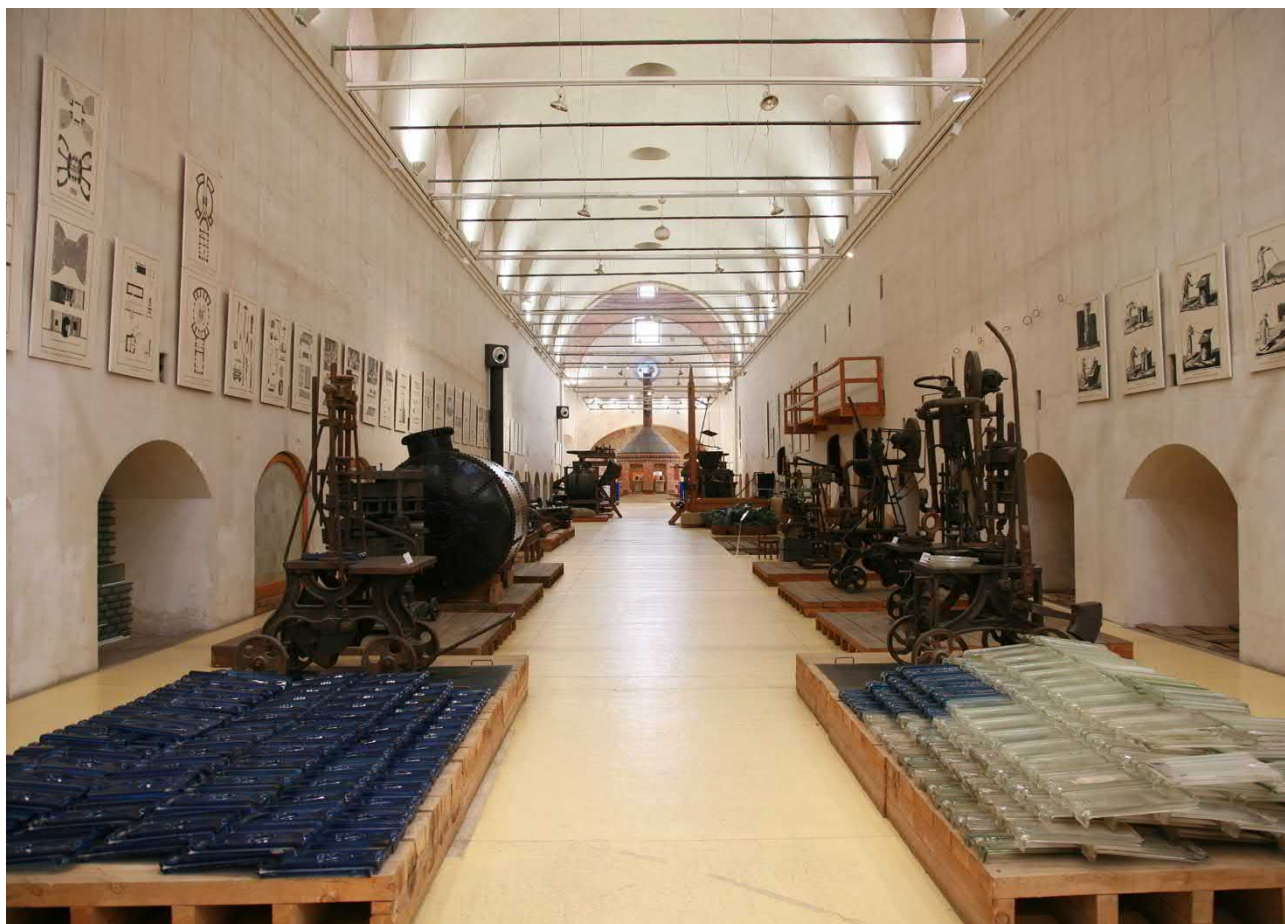


Figure 4 Technology Museum of Glass, La Granja, Spain. The Museum presents a unique assemblage of old glass factory machinery in the original space of a historical factory. *Source:* Photo: Archive of the Fundación Centro Nacional del Vidrio.

4.5 Regional and Specialized Collections

It would be an insult to call the Rijksmuseum Amsterdam a regional museum. Yet its collection of glass truly reflects the taste for glass in a specific region of Europe, namely glass *à la façon de Venise* during the Golden Age of the Netherlands in the seventeenth and eighteenth centuries. The collection's roots lie in the Netherlands Museum for History and Art in Den Haag, which was incorporated into the Rijksmuseum in 1885. Glass is also being held in the collections of other national museums, such as the National Museum in Stockholm and the Musée d'art et d'histoire in Brussels.

Quite naturally, glass museums have been established in regions that experienced a concentration of glass industry in the past. The Museo del Vetro on the Venetian island of Murano, the Museo dell'Arte Vetraria Altarese in Altare (Italy), the Musée-Atelier du Verre in Sars Poterries (France), the Glasmuseum Frauenau in the Bavarian Forest (Germany), the Broadfield House Glass Museum in Kingswinford (Stourbridge, England,

now closed, but with plans to soon reopen under a new name: the White House Cone Museum of Glass), the Museu do Vidro in Marinha Grande (Northern Portugal), and the Shanghai Museum of Glass that opened in 2011 in the former Shanghai Glassware Factory in Shanghai are prominent examples. The important place taken by Nancy in Art Nouveau crafts, namely with the Gallé and Daum factories, is being represented in the glass collections of the Musée des beaux-Arts and at the Musée de l'École de Nancy.

In some cases, glass museums emerged from a single glass factory. One of the most famous of the late nineteenth and early twentieth century, Val-Saint-Lambert in Belgium, is currently being transformed into a "Cristal Park" with new business, residential, and leisure areas [47]. The project includes "Cristal Discovery," a glass museum that was opened in 1998 in the castle of Val Saint Lambert and is currently being augmented by a glass studio [48]. The St Helens World of Glass in Saint Helens (between Liverpool and Manchester in England) is an



Figure 5 Technology Museum of Glass, La Granja, Spain. East dome of the historical factory building with model of a glass furnace.
Source: Photo: Archive of the Fundación Centro Nacional del Vidrio.

Arts center that includes a small but distinguished museum incorporating The Pilkington Glass Collection [49]. Another example is the Glasmuseum Immenhausen, which is located in the former Süßmuth glass factory near Kassel, Germany. A few of these museums grew from local collections into museums of national rank, such as the Nationaal Glasmuseum Leerdam in the Netherlands, founded in 1953; the Finnish Glass Museum in Riihimäki (Finland), which opened in 1981; or the Swedish Glass Museum in the culture park of Småland in Växjö, which reopened in 1996 [50–52].

There are also active glass companies that have a glass museum of their own, such as Lobmeyr in Vienna, Moser in Karlovy Vary, and the Museo del Vidrio in Monterrey (Mexico), which opened in 1992 in the administrative building of Vitro [53]. The most venerable glass collections linked to glass producers are to be found in the United States, however. The Toledo Museum of Art was founded in 1901 by Edward Drummond Libbey

(1854–1925), owner of one of the largest glass factories in the United States at the time. Its glass collection is small compared to those of other museums, but outstanding in quality and scope, and was moved into a separate Glass Pavilion in 2012 [54]. Toledo as the cradle of the American Studio Glass movement in the 1960s brings to mind the Museum of Glass that opened in 2002 in Tacoma, Washington, USA. It is dedicated to international Studio glass art and closely tied to the regional glass scene around Dale Chihuly and the Pilchuck Glass School [55].

Many other specialized collections are focusing on contemporary glass, such as the Glasmuseum Ebeltoft (Denmark) founded by the Danish glass artist Finn Lynggaard (1930–2011) in 1985, the Alexander Tutsek Foundation in Munich, as well as the Glass Art Centre (Cesty Skla) that was established in 2006 in the František Glassworks in Sázava (Czech Republic), to collect and display works from the International Glass Symposia (IGS) in Nový Bor. In 2008, the European Glass Museum for Modern Glass opened in Rödental (Germany) as a branch of the Kunstsammlungen der Veste Coburg (Figures 6 and 7). Whereas the historical glass collection remains on view in Coburg castle, the new museum building is devoted to the more recent history of the Studio Glass movement, in which Coburg took a special part with the Coburg Glass prizes of 1977, 1985, 2006, and 2014 [56]. The Hokkaido Museum of Modern Art in Sapporo, Japan, has given particular weight to its collection of glass from the Art Nouveau period to today since it was founded in 1977. Since then, various other museums in Japan have built significant collections of Art Nouveau glass in particular, such as the Kitazawa Museum of Art in Tokyo with its outstanding collection of glass by Émile Gallé.

It is remarkable that some of the abovementioned museums (and many more that are not listed here) act privately and receive either very little public funding or none at all. Among the private museums, two institutions stand out for their large collections: The Glasmuseum in Passau (Bavaria) was founded by the collector Georg Hörtl (1928–2016) in 1985 and is specialized in Central European glass of the eighteenth and nineteenth centuries. It owns about 30 000 vessels, of which 15 000 – a record among glass museums – are on permanent view [57]. Equally sizeable is the Hempel Glasmuseum, founded by J. C. Hempel in Nykøbing (Denmark) in 1964 [58]. It is specialized on the history of glass in Northern Europe from the Renaissance to the nineteenth century, and reaches out into contemporary art by presenting each year the Hempel Glass Prize to young Danish glass artists.

The field of stained glass is a subject of its own. The Deutsches Glasmalereimuseum Linnich (located between Aachen and Düsseldorf) is dedicated to collecting and

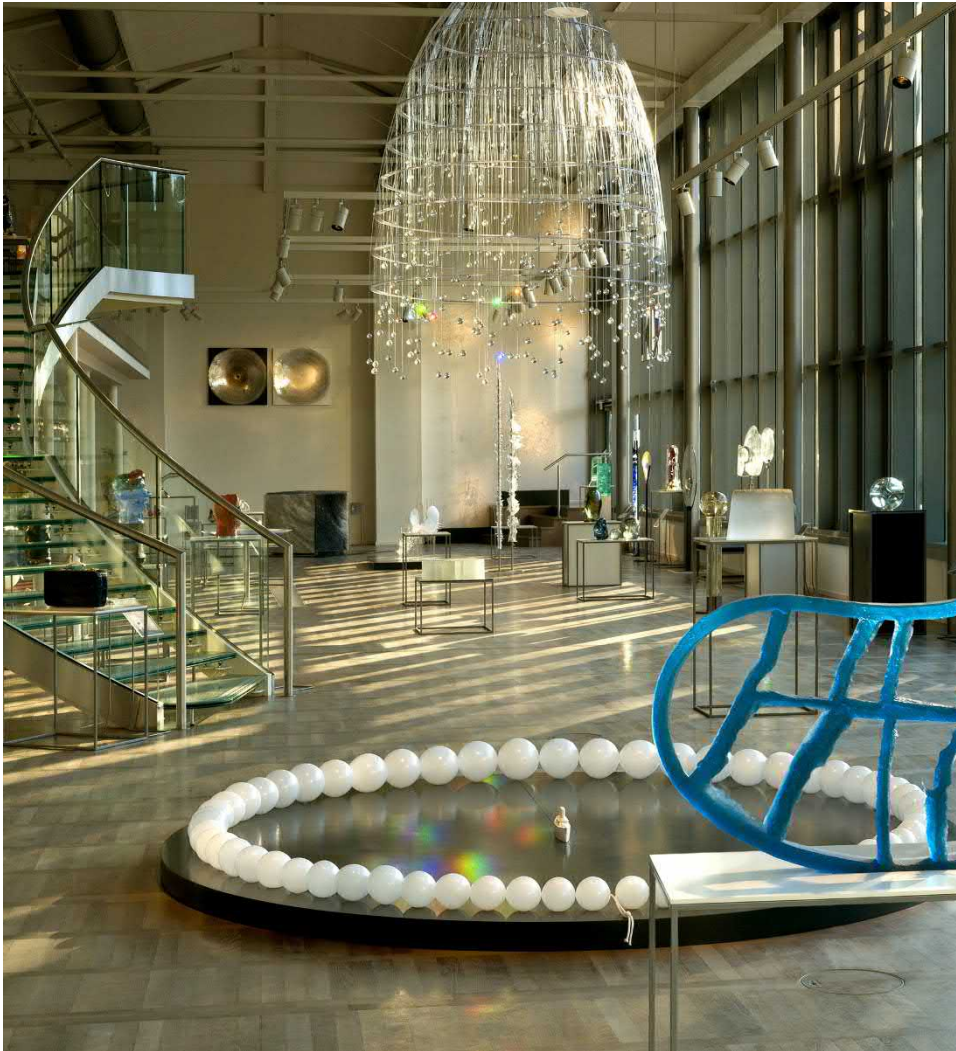


Figure 6 European Museum of Modern Glass, Rödingen, Germany. By making ample use of glass for its architecture and interior, the museum achieves a space that is uniquely transparent and full of natural light. *Source:* Courtesy of Kunstsammlungen der Veste Coburg, *Photo:* Lutz Naumann.

presenting stained glass – a rare specialization, which it shares with The Stained Glass Museum in Ely Cathedral, England. The Deutsches Glasmalereimuseum is situated in a region of stained glass production that is still active today, such as Derix in Kaiserswerth and Kevelaer, and Oidtmann in Linnich.

5 The Corning Museum of Glass

The Corning Museum of Glass is one of a kind: It is regional as well as international, combines many special collections under one roof, including a large technical section, has a significant archeological collection, and

education is one of its main priorities. Above all, it is an institution of its own, solely and entirely dedicated to the history of glass.

The museum was founded in 1951 as part of The Corning Glass Center that was built by Harrison & Abramowitz (see Section 4.4). It has always been closely tied and funded by The Corning Glass Works (today Corning Inc.) [59, 60]. It owes its existence to Arthur A. Houghton (1906–1990), one of the owners of The Corning Glass Works. Houghton had been president of the Steuben glass factory, was an expert in rare books (he endowed the Houghton Library at Harvard University), and maintained leading positions on the boards of cultural flagships such as The Metropolitan Museum of Art, the New York Philharmonic Symphony Society, and the



Figure 7 European Museum of Modern Glass, Rödingen, Germany, whose 2008 building acts as a monumental showcase. *Source:* Courtesy of Kunstsammlungen der Veste Coburg, Photo: Lutz Naumann.

Pierpont Morgan Library. Against such a background, it becomes clear that The Corning Museum of Glass was not devised as a provincial company museum. From the onset, the museum became a center for the study of glass from various periods, and has published the *Journal of Glass Studies* since 1958. The acquisition of its important glass collection was paralleled by the growth of the museum library, which was commissioned quite simply to collect every available publication on the history of glass. The library was renamed in 1984 The Juliette K. and Leonard S. Rakow Research Library of The Corning Museum of Glass, and moved into a building of its own in 2001. Today, it is undoubtedly the largest library of its kind, and it has been extended into the collection of archives and the hosting of exhibitions of its own [61].

The development of The Corning Museum of Glass and its library suffered a devastating setback in 1972, when the Chemung River flooded the town and the museum. Since then, the museum has recovered, thanks to unfailing support of the company, and undergone several expansions: 1980 (the Gunnar Birkerts building), 2001 (Smith-Miller + Hawkinson building), and 2015

(Thomas Phifer, Contemporary Art and Design Wing) (Figure 8). Today, the museum owns about 50 000 objects and welcomes about 400 000 visitors each year. With a permanent as well as a number of mobile glassmaking theaters, including demonstrations on ship cruises, with a large glass market, and with The Studio, which opened in 1996, The Corning Museum of Glass offers an experience that goes far beyond the mere display of its glass collection.

6 Glass Museums: Purpose and Concerns

The number and variety of glass museums and museal glass collections continues to grow and evolve. Many successful museums have indeed shown that glass can attract a wide range of visitors, especially if contemporary glass sculptures are on display, and even more so, if the museum offers the additional opportunity of watching glassmaking live.



Figure 8 Aerial view of the Corning Museum of Glass, Corning, New York, USA, showing the impressive dimensions of this museum dedicated exclusively to glass. To the left, the Birkerts building of 1980 with its characteristic shape that symbolizes the flow of hot glass. To the right, the annex of 2015, which replaced most of the recently closed Steuben factory. At the bottom, the main museum entrance. Source: Photo: Iwan Baan.

Visiting a museum – not only those specialized in glass – has become an event, a weekend attraction for the whole family. ICOM's definition of the purposes of a museum, quoted at the beginning of this article, mentions "enjoyment" only in third place, after education and study. But it seems that in reality, joy – or rather, the "fun" of experiencing a pleasant distraction from one's daily routine – have conquered the first place. Since the museum budgets are closely tied to the number of visitors, there is an interest to increase visitation continuously – by offering a lively program of special exhibitions and of attractive events. Museums tend to accept this development, as it helps to provide the necessary funds for the more serious aspects of a museum – acquisitions, conservation, research, and education. These pillars need to be kept solid, to avoid turning museums gradually into theme parks.

7 Perspectives

While museums are becoming more and more popular, their purpose seems less and less clear. There is a tendency toward an undifferentiated enshrinement of the

past [62]. Glass museums have the privilege to tell the world about glass. But the question needs to be raised, and answered, why the world needs to know. A strong case should be made for telling the story of a material that has accompanied mankind through most of its history of technological progress and continues to be essential for our life today.

Glass museums need to address a number of phenomena that are specific to their subject. There is, for instance, the fundamental shift of categories between the older tradition of glass vessels as more or less utilitarian things, and the advent of modern glass sculptures as works of art. A glass that has been used by a seventeenth-century Dutchman to drink beer may be acknowledged as a cultural or social document, appreciated as a good piece of design and craftsmanship, and compared to glass vessels from other periods in history (Figure 9). In the context of modern works of glass sculptures, it can even be looked at as a work of art; but such a modern projection has little or nothing to do with the original intentions of the maker and the first users. These lines can easily become blurred in the artificial settings of glass museum displays.

If we look at the older tradition of glassmaking only, we are faced with nuances that pose a challenge even to the



Figure 9 Beer glass, reputedly found in Dordrecht, The Netherlands, probably made in Rotterdam, first quarter of the seventeenth century. Kunstpalast, Glasmuseum Hentrich (Gl 2011–2026 e). Source: Photo: Kunstpalast.

expert. To distinguish vessels that were very common and ordinary in their time from the more exceptional masterpieces can be quite difficult. Moreover, the common vessel could have traveled into a different cultural context and thus become a precious rarity after all. How should this and much more be communicated to the visitor?

As for modern glass art, there is a tendency among glass museums to compete in collecting Studio glass; and glass artists, steadily growing by number as well as by quality of craftsmanship, continue to cater to this demand. There certainly is a worldwide fashion, perhaps even a Studio glass craze. But looking ahead 20, 50, or 100 years of time: Will people then consider the vast accumulations of glass art a boon, or a bubble?

Concerns such as these make clear that glass museums, as everything else, must change over time, in order to keep their attractiveness to the public. But glass is a material that has caught the curiosity and imagination of the people for millennia, and still continues to provide a great technological challenge and potential. We can trust that it

will continue to provide plentiful fascinating content for the glass museums of the future.

Acknowledgments

This contribution has been sent to all members of the ICOM Glass committee. I received valuable input from my glass museum and glass research colleagues and thank in particular Milan Hlaveš, Reino Liefkes, and Teresa Medici, as well as Ayşegül Cihangir, Karin Dalskov, Susanne Evers, Eva-Maria Günther, Giulia Musso, Eva Nováková, John Parker, Paloma Pastor Rey de Viñas, Michel Polfer, Ulrike Scholda, and Hana Wollerová.

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11.1

Postface – A Personal Retrospective

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As I look over the tremendous outpouring of intellectual effort, from talented scientists across the world, that has produced the contents of the *Encyclopedia*, I am humbled by the assignment I accepted to write, namely some concluding retrospective – something that might capture the essence of this science of glassy matter (and the liquid states that preceded them in most – but certainly not all – cases). It is a field so rich in content that it is small wonder that it holds the attention of nearly all who venture into it.

The author has had the privilege of working, now over a 60-year timespan, in a variety of aspects of the physics and chemistry of glass-forming liquids and their solid products where a particular condition of the liquid has become frozen in time and space by its glass transition. I still remember the sense of wonder I felt when, as a fresh PhD, I tested for myself the comment of David Turnbull, based on reports from Russian scientists, that certain mixtures of the simple salts, KNO_3 and $\text{Ca}(\text{NO}_3)_2$, yielded clear glassy solids when cooled from their liquid states. What could be simpler than a liquid with two cations, each with the argon electronic structure, and a compact triangular anion that compensates their positive charges? Where were the networks, or polymers, that I had always read were necessary to frustrate the crystallization process? And yet there it was. One could watch the rapidly increasing viscosity as the liquid cooled, and could pull beautiful long fibers from this collection of simple ions (*ionic argon*). Surely the viscous liquid and glassy states must be fundamental to understanding the physics of the liquid state that so many considered to end at the melting point. I became a life-long devotee of glass-forming liquids, and still salivate when I read of some synthesis that is producing an *oil*.

How strange it is that a liquid need only be 100 times as viscous as water at its melting point, to have difficulty crystallizing when cooling at moderate rates (e.g. in a vial plunged into liquid nitrogen for molecular liquids, or as a liquid poured onto a cold metal plate for higher-temperature systems), but then it requires another 13 orders of magnitude change in viscosity before the liquid can no longer adjust its structure to the decreasing temperature, and so gets “frozen in space-time” as a glass.

Sixty years amounts to some 12 generations of graduate students. Clearly there have been huge developments in the field in this period. The contents of the *Encyclopedia* stand as testimony to those advances, some of which would have been totally unexpected, whereas other have been more incremental, pushed by newly recognized needs.

Sixty years ago, the formation of bulk glasses from liquid metals was unknown, indeed the formation of *bulk* glasses that are metallic is of very recent origin. They were first reported in 1990 [1] by A. Inoue, coauthor of Chapter 7.10 on the subject in this volume.

Sixty years ago, the ability to simulate the formation of glassy states with fast digital computers was only a dream. It is now 40 years since first attempts to simulate the archetypal glass former SiO_2 were made with pairwise additive interaction potentials [2]. Chapter 2.9 by Kob tells how different things are now.

Silica glass is a remarkable material, which we have learned to pull into (polymer-protected) fibers of essentially theoretical strength. How could we imagine, 60 years ago, that our world would be connected by glass fibers of this composition, carrying information from one continent to another at the speed of light (in glass). It has been as major a revolution as that brought about by the harnessing of radiowaves much earlier.

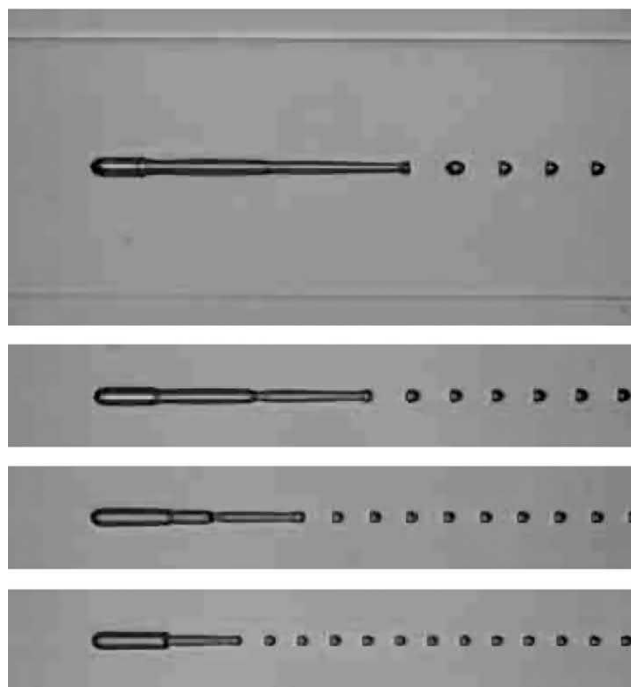


Figure 1 Line of *bullet* voids in the center of the silica core of an optical fiber, resulting from passage of the 6000 K, ~5 GPa plasma through the fiber. The density and related properties of the residual silica have yet to be determined. *Source:* Reprinted with permission from [4] © Optical Society of America.

Another, more esoteric and so far little recognized, consequence of the science of optical fibers from silica (with claddings of Ge-doped silica that confine the transmitting energy to the core of the fiber), has been the fabrication of a mini-laboratory for potential ultrahigh temperature and pressure science. This has been demonstrated by Kashyap and coauthors [3] following their findings of the *optical fiber catastrophe* in which a plasma, initiated by a defect or a blockage in the fiber, ignites and moves back through the fiber toward the light source at a velocity controlled by the fluence, creating briefly a zone of temperature in excess of 5000 K (depending on the fluence) and enormous pressure confined by the cladding, which can evidently withstand some 7 GPa (Figure 1) [4, 5].

This observation bears on one of the really unexpected things that has happened, in the second half of our 60 years – and one that is still a subject of much controversy. This is the finding that certain glass-forming substances, pure substances, can form more than one sort of glass. Called *polyamorphism*, this is now well established as a phenomenon in computer-simulation studies [6, 7], but remains subject to much uncertainty in laboratory studies, mainly because of its close (and understandable) association with crystallization [8]. There is a nice

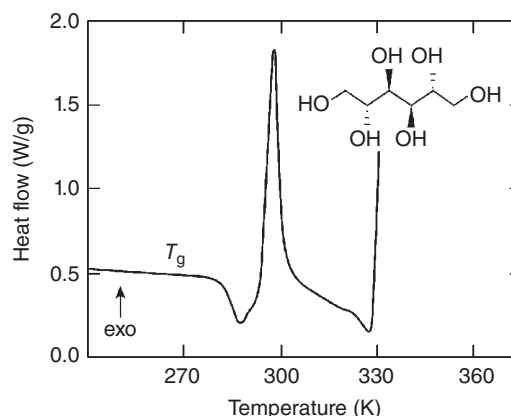


Figure 2 Enthalpy spike occurring just after the glass transition of quenched D-mannitol, producing the second amorphous phase whose X-ray radial distribution function (Figure 3) is virtually identical to that of the initial glass, and totally distinct from that of the crystal.

Chapter 3.9 on the subject by McMillan, who coauthored the first paper on this phenomenon after Mishima's seminal observation on glassy water [9].

The most recent (and perhaps the cleanest) example may be that involving a polyalcohol (D-mannitol, an optical isomer of the much-studied 6-carbon, 6-alcohol sorbitol). D-mannitol needs fast quenching to vitrify, but then, during reheating through the normal T_g , it transforms sharply to a second more stable glassy form that has a lower density (Figure 2) [10, 11]. The two different glasses of the same substance have almost indistinguishable XRDs (Figure 3) but rather different enthalpies [10]. When converted to an entropy and inserted into the well-known Adam–Gibbs equation,

$$\tau = \tau_0 \exp(C/TS_c), \quad (1)$$

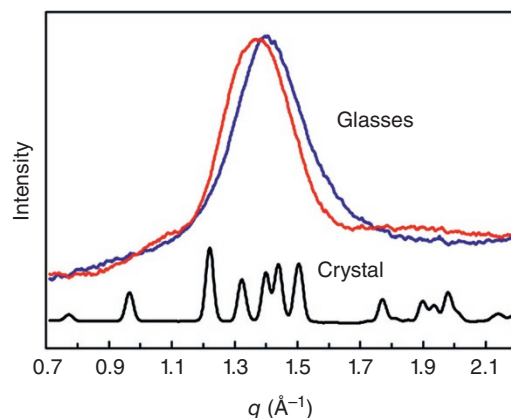


Figure 3 The X-ray diffraction patterns of D-mannitol in the crystalline and two different amorphous states separated by the first-order transition seen in Figure 2. *Source:* After [10].

the decrease in enthalpy observed surprisingly implies that the second polymorph formed in the transition should have a relaxation time orders of magnitude longer than that of the parent liquid – which means far longer than that of the first glass at its glass transition temperature. How could this happen? The answer should be that it is the result of the nucleation of a phase having a substantially lower chemical potential than that of the phase from which it nucleated. As a result, diffusion across the phase boundary would be a much faster (free energy *downhill*) process than diffusion within the body of the first glass formed.

Another and possibly related finding of high interest has been that, in a majority of glass formers of the molecular variety, one can obtain in an unexpected way, glasses (necessarily in small amounts) of very different properties – like those of glasses that would be formed by millions of years of slow aging. Here, vitrification proceeds via vapor deposition onto a substrate whose temperature is controlled to lie a short distance below the normal T_g . This discovery by the Ediger-Yu groups [12], who named these materials *Ultrastable glasses*, was initially reported for the large organic molecule tri- α naphthyl benzene (Figure 4). It has since been reported also for a large number of organic glass-formers – but so far no inorganic cases. Since the ultrastable glasses have much higher moduli than their “normal” glass brothers, the prospect of making inorganic glassy films of high scratch resistance would seem to be an objective worth pursuing.

It is still unclear whether ultrastable glass formation is a phenomenon limited to glass formers of fragile character or not. Something very different happens in the case of the intermediate (hydrogen bonded) liquid glycerol [13] and some relatives, whereas no such behavior is seen in the case of water, which is a very strong liquid near the glass transition.

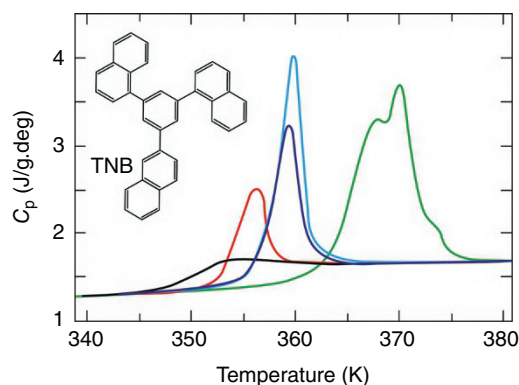


Figure 4 First demonstration by differential scanning calorimetry of the large enthalpy deficit and relative kinetic stability of an ultrastable glass of tris-naphthylbenzene. Source: After [13].

These features remind me of the breakthrough in the problem of residual entropy of ice, due to proton disorder, that was largely resolved by the famous work of Suga and coworkers. These authors [14] found a way to unlock the kinetics of transition to a lower entropy (proton-ordered) state of the ambient-pressure ice crystal. It seems obvious to me that if such a state exists, the fastest way to reach it must be by a process of nucleation and then growth down the free energy gradient. But what is this if it is not polymorphism? We await transmission electron microscope studies of the early stages of growth of the ultrastable glass films. We already know that, in thick films of these glasses, the way back to the normal viscous liquid state is by this mechanism.

This latter may seem like an esoteric matter, but in these days of increasingly nanoscopic technology, it might be of vital importance. It is reported [15] that limitations on the fidelity of nano-mechanical and electro-dynamical devices are set by the white noise associated with the boson peak modes which, like the cryogenic anomalies, are greatly diminished in the ultrastable glass state. All indications are that this state is just a less disordered version of the normal glass, though there is some debate about the mechanism by which it is accessed. It is not necessarily a denser state, in fact the most nearly perfect glasses, in the sense of those with the least evidence of defects and excess entropy, are those with low-density open network structures, like water and a-Si. Hopefully, the future will yield a better understanding of the *perfect* glass state, and its accessibility or otherwise [15, 16]. From recent studies [17], it also seems possible that this sort of transition, although weaker and higher in temperature, is involved in the mechanism for fast digital switching in the so-called Phase Change Materials, which are obtained from a range of weakly metallic chalcogenide liquids that become semiconducting glasses on hyper-quenching and well-conducting crystals on controlled reheating – and are under development for ultrafast rewritable computer-memory technology.

And of course there were always “theories of glass” of different qualities. Despite all the progress that has been made, most would agree that we still do not have a satisfactory theoretical understanding of the process of vitrification, or why it occurs so suddenly in some liquids, the so-called *fragile* (or *short*) ones, and over such a relatively wide temperature range in other cases, like the archetypal *strong* (or *long*) glass former, SiO_2 . Diverging length scales have been popular as a concept but these are only proposed for four-point correlation functions that cannot be measured in the laboratory [18]. It does not help that the static quantity, the mean-square volume fluctuation derived from the measured isothermal compressibility from the Landau relation,

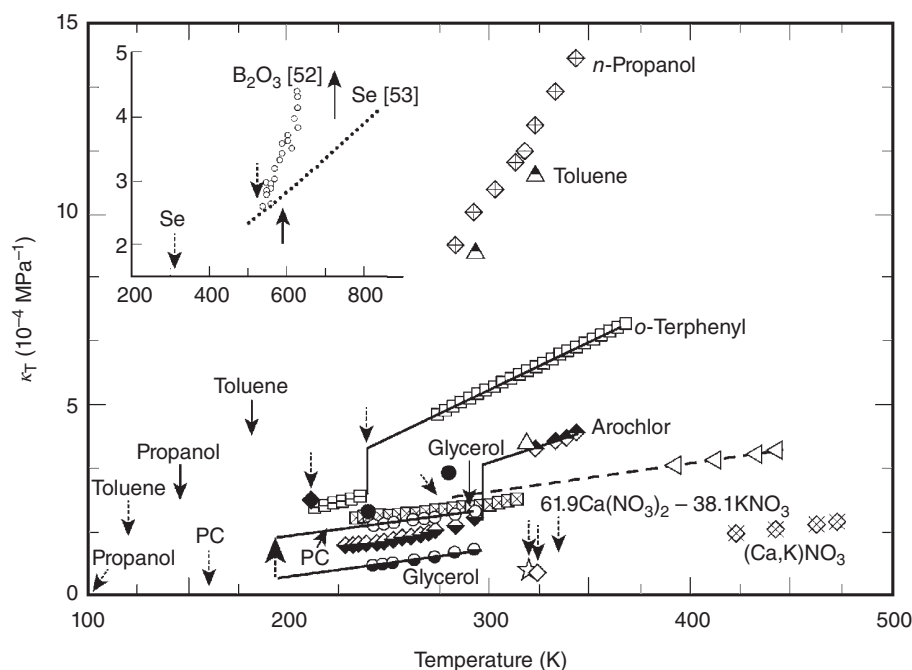


Figure 5 Isothermal compressibility data for various glass-forming liquids of organic and inorganic types, showing a consistent downward trend with decreasing temperature (Source: After [19]). Solid arrows: melting temperatures of crystals; dashed arrows: glass transition temperatures; PC: polycarbonate; star: 45 $\text{Cd}(\text{NO}_3)_2 \cdot 45 \text{KNO}_3$ at T_g ; (Ca,K) NO_3 : 61.9 $\text{Ca}[(\text{NO}_3)_2] \cdot \text{KNO}_3$.

$$\kappa_T = -1/V(\partial V/\partial P)_T = -\langle(\Delta V)^2\rangle/Vk_B T, \quad (2)$$

decreases with temperature as T_g is approached (Figure 5) for all the glass-forming liquids for which we can find data [19]. It implies that a static correlation length in all cases decreases going into the glass transition. This applies to the archetypal glass former, silica itself, in the observable range, though simulations suggest it may have an anomalous range at temperatures above that of its heat capacity maximum at $\sim 4500 \text{ K}$. Only occasional *anomalous liquids* like water and liquid tellurium (which are both exceptionally bad glass formers, i.e. especially fast crystallizers), behave otherwise in their observable temperature ranges [20]. But even these liquids would be expected to become *normal* at lower temperatures when approaching the glass transition if crystallization could be avoided.

Before leaving this retrospective, we should consider the limits on what sort of materials we are prepared to recognize as glasses for future consideration in our field. It is well known that there are important ergodicity-breaking phenomena in the field of magnetism and that spin glasses are a heavily researched subject for which advanced theories are available. However, the physical interactions between the elements of that class of substance are so different from those that determine the phenomenology of our field that I do not see much benefit in including their consideration in a work of this type. On the other hand, the research area of

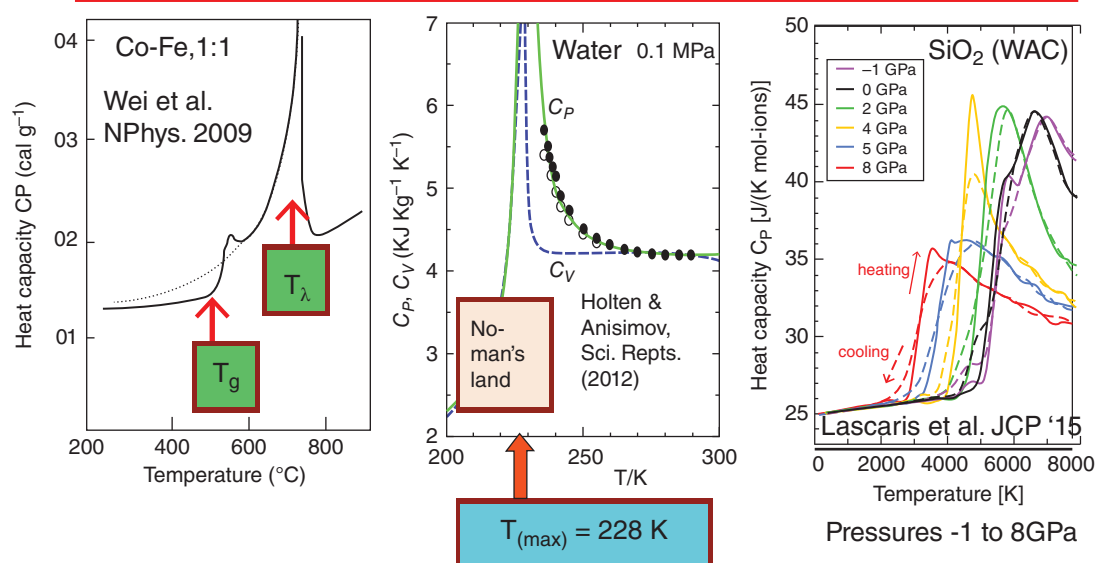
orientationally disordered crystals seems highly relevant. These materials also conform to a strong/fragile pattern but, in contrast to glass-forming liquids, most examples fall at the *strong* end of the spectrum. Many prove to be just the low-temperature end of an order-disorder transition, which is very suggestive [21]. A good example of a classical order-disorder transition, interrupted by a “glass” transition is that of the bimetallic Co–Fe system depicted in the left-hand panel of Figure 6 for which the glass transition kinetics proves to be strictly Arrhenius, like that of an ideally “strong” liquid [22]. Likewise, we have been able to learn a lot from the study of colloidal systems, even though the interactions between particles are very different from those in structural glasses and temperature does not play the critical role we are accustomed to. Certainly these systems have ergodicity-breaking, and crystallization, as key phenomena, just as do our structural glasses. A chapter on these relationships in some future edition of the *Encyclopedia* would probably be valuable. In the same spirit, the cover page of the issue of *J. Phys. Chem. Glasses* for the Sheffield meeting celebrating the centenary of the Society of Glass Technology (Figure 6, which is taken from the opening talk of the Turner Symposium abstract) is indicating a willingness to consider glass transitions with suggestive forms in materials outside the norm of glass-forming systems.

Looking forward, there is nothing more certain than that there will continue to be surprises. Of high

PHYSICS AND CHEMISTRY OF GLASSES

European Journal of Glass Science and Technology Part B

Critical points in systems with glass transitions



100 Years of the Society of Glass Technology

Figure 6 Cover page of the centennial issue of the Glass Technology Society, featuring a figure from the Turner Symposium opening talk illustrating glass transitions in nonclassical systems with apparent critical or near-critical behavior. Source: Reproduced with permission of the Society of Glass Technology.

probability will be the finding of inorganic equivalents of the ultrastable glasses mentioned above, which have so far only been reported for molecular liquids that are fragile relative to the common inorganic glasses. Some of the less common high-modulus inorganic glass formers such as calcium aluminate and lanthanum borate [23] are very fragile in their liquid states and would make good candidate materials for ultrastable glass formation by sputtering onto hot sub- T_g substrates. Thin films of such materials could provide very high-modulus protective coatings and low-noise substrates for nano electronic devices. At a fundamental level; the enthalpy of solution of an ultrastable glass of composition near that of YAG

garnet (e.g. in the work of Navrotsky [24]) would be of high interest in the context of understanding the *perfect glass* problem [15].

Given the extraordinary interest in reticular chemistry generated in the last two decades [25], it will be surprising if some all-inorganic vitreous analogs that yield continuous films of high porosity at the nanometer scale, suitable for gas separations and other purposes, are not developed, though the high-temperature stable templates needed for their formation might be difficult to find. Active research in the field of "g-MOFs" is just beginning.

Also one might expect more interest in variable band-gap glasses formed by chemical vapor deposition on

controlled temperature substrates of compositions of similar crystal structure like the 3–5 and 2–6 wurtzite structures, e.g. GaN and ZnO, to cover the solar spectrum with weather-resistant photon absorbers. There are a large number of such open network structures that can be incorporated into such structures. Their mixtures should be much more tolerant of mismatch strain than are their crystalline equivalents. Likewise, the composition-dependent metal–semiconductor transitions in chalcogenide glass formers will lend themselves to further exploitation in the lower frequency domain.

Anything that one can try and guess at, here, will surely miss the mark of the important things to come from future generations of glass scientists, but one thing that we can be sure of is that those working in the field and making the new discoveries will feel as privileged to work in it as have we, i.e. those who have participated in the production of this *Encyclopedia*.

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